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ELEMENTARY THEORY
OF
QUALITATIVE ANALYSIS

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James Kendall, Editor

ELEMENTARY THEORY OF QUALITATIVE ANALYSIS

BY

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FOREWORD

In ten years of teaching the theoretical side of qualitative analysis to freshmen and sophomores, two facts have come quite noticeably to the attention of the writer. One is that, when using texts in which there was little or no treatment of the theoretical matter, the students have consistently asked where they could find a consecutive, unified treatment of analytical theory in written form, to supplement their lectures. Until recently there have been no such texts of an elementary nature.

The second fact is that, in such texts as have a fuller treatment of the theoretical matter, little or no attention has been paid to its application. Students seem to grasp the principles involved in the concepts of the Law of Mass Action, Equilibrium, and the like, but the application of these principles to the diversified cases which arise seems to leave them at a loss. In the first place, every problem seems to them to be an individual one rather than an example of one of a few types, and in the second place they do not seem to know where to begin the attack on a given problem. With a view to meeting these two needs, the writer presents the following treatment of the subject in such a fashion, it is hoped, that it may be used to supplement the practical material in any laboratory manual the teacher prefers to use.

Still another idea has been kept in mind. For courses of sufficient length and student preparation to warrant it, a somewhat more detailed treatment has been given in certain phases of the subject. Thus, a chapter on atomic structure and crystal structure has been included, along with a brief

treatment of the methods of measuring and calculating the degree of dissociation of electrolytes, with illustrative problems. Calculations and problems to illustrate the value and practical use of the Law of Mass Action and the Solubility Product Principle have also been included, but in no case is the treatment extensive. Should the teacher feel that the nature of the course does not warrant the inclusion of such detail, these parts may easily be omitted and the subject treated from a purely qualitative and non-algebraic point of view.

F. W. M., Jr.

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ELEMENTARY THEORY OF QUALITATIVE ANALYSIS

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CHAPTER I

CRYSTAL STRUCTURE AND ATOMIC STRUCTURE

Introduction. — Whereas it may seem that there is little connection between the structure of atoms and crystals and the explanation of the phenomena occurring in analytical chemistry, yet it is essential that a student have a working knowledge of crystal structure in order to properly understand the phenomena of ionization. In addition, a good grasp of the electron theory helps the student a great deal in understanding oxidation and reduction phenomena. With a view toward establishing the fundamentals of these two ideas, the following material is presented.

X-Rays and Electrons. — To pass an electric current across a gap of air, particularly if that gap is eight or ten inches long, requires a very high electromotive force and the resulting spark is irregular and zigzag. If the terminals from which the spark is coming are inclosed in a glass bulb and the pressure in the bulb is lowered by withdrawing air (such a device as this is called a vacuum-tube or Crookes tube), it becomes increasingly easier to make the spark cross, until, at fairly high vacua, there is a steady luminescent stream across the gap. The whole tube then glows with a rather eerie greenish light. Further evacuation results in an increased resistance to the passage of the current.

Sir William Crookes discovered in 1874 that if an opaque object were placed in the path of the luminescent stream, a

shadow was cast on the opposite wall of the tube. A piece of platinum placed in the stream became red-hot. A strong electromagnet placed with one pole on either side of the stream, outside the tube, deflected the stream toward the positive pole. From these observations it was concluded that the luminescent stream was made up of negatively charged (attracted to the positive pole) material particles (heating of the Pt due to bombardment), traveling at high velocities. These particles, formerly called *cathode rays* because they seemed to come from the cathode in the tube, were studied carefully by several men, among them J. J. Thomson. The latter called them corpuscles. Later Storey suggested the name *electron*, which is now used exclusively. These electrons occur in the vacuum tube regardless of the nature of the electrode. It was concluded, therefore, that they were common to all matter. Subsequent careful study of the electron has led to the conclusions that the electron is nothing but a negative charge of electricity equal to 4.774×10^{-10} electrostatic units and that it has a mass about $\frac{1}{1867}$ that of the hydrogen atom.

The fact that the electron exists in the tube proves that there must be a positively and equally charged body to counterbalance the charge on the electron. Such bodies do exist and are positively charged atoms of the residual gas in the tube. As will be apparent later, the atoms of the gas have lost an electron each by collision with the electrons from the cathode, and by virtue of this loss have a positive charge in excess. The positively charged atoms of the gas are called *canal* or *anode rays*. They travel much more slowly than the electrons because they have a much greater mass. The fact that they are positive may be demonstrated by their deflection in a strong magnetic field.

Vacuum-tubes were used for some twenty years before it was accidentally discovered that there was something happening outside of the tube as well as within. In 1895,

Röntgen discovered that there were rays of some type coming through the glass. Not knowing what they were, he called them *X-rays*. They are also sometimes called *Röntgen rays*. These rays have since been investigated and found to have rather remarkable properties, of which advantage is taken in the present-day X-ray machine. Figure 1 shows a standard type of X-ray tube.

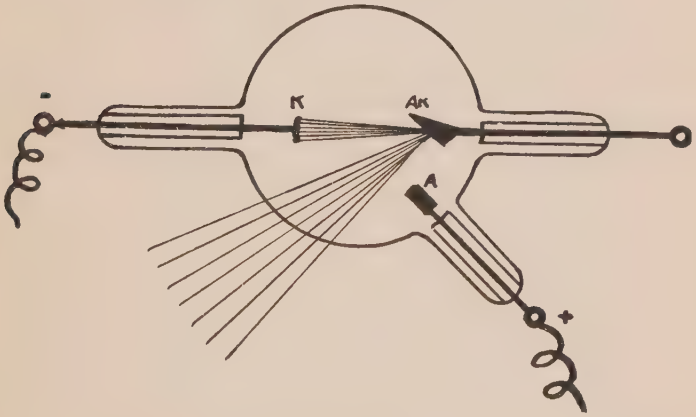


Fig. 1
Vacuum-Tube

The tube is made of glass. It is evacuated to about $\frac{1}{1000}$ of a millimeter of mercury, the metallic electrodes being sealed in the glass as shown. A current of high potential enters at the anode (A) and leaves at the cathode (K). The electrons impinging upon the anticathode (Ak) give rise to X-rays which are invisible. The X-rays pass through the walls of the tube.

Properties of X-Rays. — As before stated, X-rays have remarkable properties. They have been very important factors in some of the most fundamental discoveries concerning the nature of the atom. Whenever swiftly moving electrons

are made to impinge on some object, X-rays are generated. These X-rays are the same in nature as light-waves except that the wave-length of the former is much shorter. The generation of X-rays may be looked upon as being somewhat similar to the formation of light-waves from a hot body. It has been clearly demonstrated that radio-waves, light-waves, and X-rays are all electromagnetic waves varying in wave-length only.

Perhaps the most remarkable property of X-rays is their penetrative ability. They are able to pass through glass, as we saw above, and through wood or flesh. In addition, they are able to affect a photographic plate and it is from this that their great usefulness comes. When X-rays are passed through media of different densities, through flesh and bone, for instance, the latter, being denser, prevents the passage of the rays more than does the flesh. The result on the photographic plate is that where the bone has prevented the passage of some rays, there is less effect upon the plate than in the flesh section, and a shadow-picture of the object is taken. We are all familiar with the value of the X-ray photograph in surgery, dentistry, and medicine.

X-rays also have a peculiar ability to knock electrons loose from atoms. Thus, as has been shown, if a gas is subjected to X-ray treatment, electrons are expelled from the atoms of the gas as a result of the intense jar of collision with the X-rays. The atom of the gas with one or more electrons knocked out is now positively charged, as may be shown by means of an electroscope. This phenomenon reminds us of the dissociation of electrolytes in solution, except that in this case no collision of X-rays is necessary. We will see later that the two phenomena are actually the same in principle.

X-Ray Spectra. — Knowing that light-rays and X-rays are vibrational phenomena of the same type, we should expect

them to show somewhat similar properties. (The wave-length of light is about 1,000 times greater than that of X-rays.) It is well known that if a metal mirror is ruled with from 50,000 to 100,000 lines to the inch, it will, as a result of interference phenomena, resolve white light into its spectrum. The number of rulings on the grating is determined by the wave-length of the light. Now, since X-rays have a wave-length about $\frac{1}{1000}$ that of light, we should be able to get an X-ray spectrum if we can get a grating with rulings about $\frac{1}{1000}$ the distance apart of those on the light-grating. It is not humanly possible to rule 50,000,000 lines to the inch, but it occurred to Professor Laue in 1912 that if crystals were made up of orderly rows of atoms, as their beautifully symmetrical structure indicated, these rows should be about 1,000 times closer together than the rulings on a light-grating, and should, therefore, give X-ray spectra. Experiment corroborated his hypothesis.

In a light-grating, all the lines causing diffraction are obviously in the same plane, and the patterns obtained as a result of the breakdown of light are relatively simple. In the case of crystals, the rows of particles do not lie in the same plane. As a result, there is reflection and diffraction at each successive plane of particles and a much more complex pattern results. Since the principles involved in the study of crystal structure are rather complex and difficult, no further discussion of it will be attempted here.* Suffice it to say that there are some 320 possible crystallographic arrangements apportioned into seven systems of symmetry and thirty-two classes of crystals. The space-patterns of these crystals are best interpreted by assuming that a series of contiguous small cubes are formed by the intersection of

* For a more detailed discussion in simple form see Kendall, *Smith's Inorganic Chemistry* (1926), p. 64 *et seq.* For a complete discussion, see W. H. and W. L. Bragg, *X-Rays and Crystal Structure.* Since the Smith-Kendall text is referred to frequently in what follows, it will be designated simply as "*S-K*, p. —."

parallel planes within a large cube. All the possible arrangements of the atoms within the crystals may be inter-

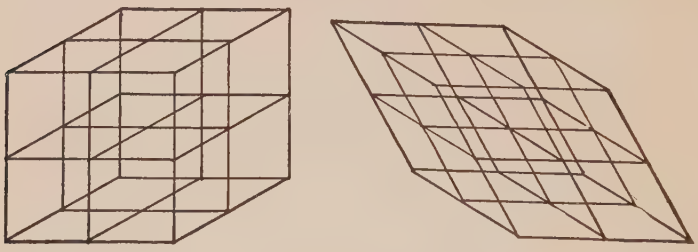


FIG. 2

SPACE-LATTICES

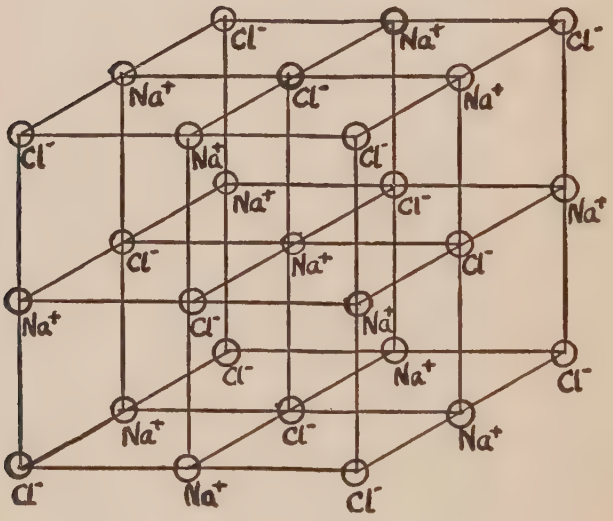


FIG. 3

STRUCTURE OF SODIUM CHLORIDE

preted in terms of different configurations of these small cubes, called "space-lattices." Figure 2 illustrates these types. Let us consider one well-known example which will

bring out a fact of considerable importance in the theory of ionization.

In common salt the arrangement of atoms has been found to be as indicated in Figure 3. Instead of being made up of molecules of NaCl, as was commonly thought, the crystal is made up of positively and negatively charged atoms of sodium and chlorine respectively and there is *no actual combination.* The atoms of Na^+ and Cl^- are not really so far apart as is indicated in the diagram. They are so drawn for the sake of clarity.

There is no specific relationship between any two atoms within the crystal to the exclusion of others. Each positively charged atom of sodium is surrounded by six negatively charged chlorine atoms; each negative chlorine atom is surrounded by six positively charged sodium atoms; and the whole is apparently held together by the electric forces originating in the exchange of charges. We can consider that a sodium atom has given up a negative charge (electron) to the chlorine and has itself become positively charged as a result. After we have studied the structure of the atom in detail, the above statements will have more significance.

Radioactivity. — Becquerel, a French physicist, in investigating fluorescent substances to find if they gave X-rays, discovered that uranium salts affected a photographic plate through its black paper covering in the same way as did X-rays. This led to the discovery that all uranium salts gave off penetrating rays. At Becquerel's suggestion, Mme. Curie carried the investigation of these active minerals further and discovered that certain uranium ores containing relatively little of that element were much more active than a pure uranium salt. This led in turn to the discovery of radium, an element about 2,000,000 times more active than uranium.

Since that time several other so-called "radioactive" substances have been found and extensively studied. They

all have the property, which as yet has not been controlled in any way by man, of giving off rays of three types, though but few of them give all three. The three types of rays have been called α, β, and γ rays, and are similar in character to the canal rays, cathode rays, and X-rays respectively, of an X-ray tube.

Alpha Rays. — These rays are positively charged particles traveling at enormous rates of speed. Rutherford has shown that these α particles are charged positively with a charge equivalent to that of two electrons. Thus, when two electrons come in contact with an α particle, its charge is neutralized and an atom of the gas helium is formed. It appears, then, that α particles are atoms of helium gas which have lost two negative charges (as will appear later, they are made up of four + and two − charges). The α rays correspond to the canal rays of the vacuum-tube, except that the latter are much less speedy and vary in size, whereas α rays are all of the same size.

Beta Rays. — These correspond to the cathode rays of the vacuum-tube and are unit negative charges of electricity or, in other words, electrons. They travel at much greater rates of speed than do cathode rays. They are, consequently, much more penetrating.

Gamma Rays. — These are identical with X-rays except for shorter wave-lengths. They are probably produced by the impact of the β rays on surrounding matter. This is evidenced by the fact that the γ rays never occur in an element which does not give β rays. We must keep in mind the fact that while the rays emanating from radioactive elements are of three kinds, each element does not give all three. The emission of all three is the exception rather than the rule.

The Structure of the Atom. — Discovery of the electron and the facts of radioactivity contributed greatly to the

problem of elucidating the structure of the atom.* The fact that the electron or β particle had the same charge and mass (0.00054 = $\frac{1}{1867}$ of the mass of an H atom), regardless of what element it came from, was a significant indication that all elements contained electrons. The same was true of α particles. No matter what radioactive element was studied, if it gave off α particles, they were all identical. These facts and many others which could not well be included here led to the present-day theory of the structure of the atom.

J. J. Thomson was the first to suggest that the atom was made up of electrons distributed through a sphere of electricity. In 1911, Rutherford, accepting the fundamental idea that all atoms were made up of positively and negatively charged particles (now called *protons* and *electrons*) of electricity, suggested certain alterations in Thomson's theory. Rutherford postulated a central positively charged nucleus surrounded by planetary electrons, in the fashion of our solar system and similarly spaced, i.e., the electrons at relatively large distances from the nucleus and from each other. The central positively charged nucleus represents almost the entire weight of the atom, whereas the planetary electrons lend to the atom its volume. The experiments to support these ideas were somewhat as follows. Rutherford and his co-workers bombarded very thin sheets of metal with the positively charged α particles from a radioactive material. They demonstrated that some of these α particles would have to pass directly through some of the atoms of the metal. In so doing, it was observed that these α particles suffered wide deflections from their original paths. This pointed very definitely to the fact that the positive charge of the α ray had met a strong repelling (and therefore positive) charge. This led to the conclusion that the positive charge in the atom was greatly concentrated in what is now called the nucleus. From the data obtained, it was calcu-

* *S-K*, p. 518 *et seq.*

lated that the mass of this nucleus represented almost the entire weight of the atom and that the charge on the nucleus was equal to the charge on the planetary electrons multiplied by a number which was approximately one-half the atomic weight of the element.

Since the successive atomic weights of the elements vary by approximately two units, it was suggested by van der Broek that the electronic charge be multiplied by the number representing the order of occurrence of the element in the periodic system starting with hydrogen. This would give a number approximately equal to the atomic weight over two. That this suggestion had a rather startling substantiation in the actual make-up of the atom will be seen in the work of Moseley on atomic numbers. Of course it should not be thought that the suggestion of van der Broek was entirely fortuitous, because it had been felt for a long time that there must be something more fundamental than the atomic weight connected with the structure of the atom.

Atomic Numbers. — By using the crystals of different elements as the anticathode in an X-ray tube, Moseley in 1914 showed that they emitted X-rays with frequencies characteristic of each. The radiations characteristic of each element occur in two series, called the *K* and *L series*. It was found that the frequencies varied by a constant amount as successive elements in the periodic table were studied, and if these frequencies are plotted for successive elements, a result similar to Figure 4 is obtained.

Moseley found too that, if the square of the frequency was plotted against the atomic weight, no great regularity was evident; but if the number representing the order of occurrence of the element in the periodic table (calling hydrogen 1) was substituted for the atomic weight, an excellent straight-line graph was obtained. Moseley decided that the atoms of the elements varied from one to the next by a

constant quantity which he called Q. Let us quote his own words:

"It is at once evident that Q increases by a constant amount as we pass from one element to the next, using the chemical order of the elements in the periodic system. . . . While, however, Q increases uniformly, the atomic weights vary in arbitrary manner. . . . We have here a proof that there is in the atom a fundamental quantity which increases by regular steps as we pass from one element to the next. This quantity can only be in the charge of

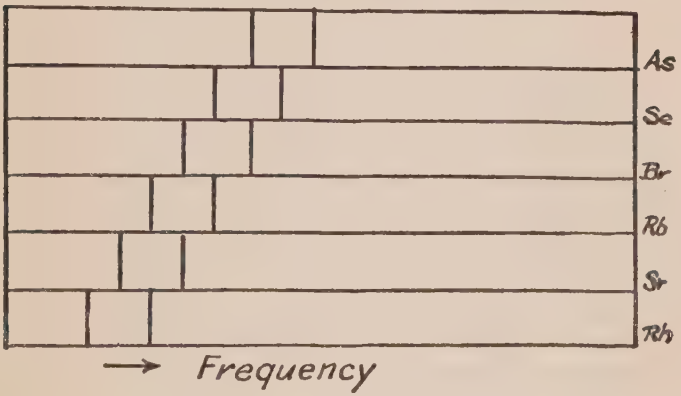


Fig. 4

K Series (Diagrammatic) for Elements As to Rh

the central nucleus, of the existence of which we have definite proof. Rutherford has shown from the magnitude of scattering of α particles by matter that the nucleus carries a positive charge approximately equal to A/2 electrons where A is the atomic weight. . . . Now the atomic weights increase on the average by about two units at a time, and strongly suggest the view that the quantity Q increases from atom to atom always by a single electronic unit. We are therefore led by experiment to the view that Q is the same as the number of the place occupied by the element in the periodic system. This **atomic number** is then for H, 1; for He, 2; for Li, 3, etc."*

* See *S-K*, inside back cover, for atomic numbers.

An Epitome of Current Ideas Concerning the Atom. — From the facts quoted and other data too numerous or complex and lengthy to cite, the following conclusions regarding the structure and properties of the atom have been reached and almost universally accepted:

1. That atoms are made up of positive and negative charges of electricity.
2. That the positive charges are concentrated in the nucleus.
3. That, excepting hydrogen, the nucleus also contains electrons, but that the positive charges (called *protons*) are in excess.
4. That the excess protons of the nucleus are electrically neutralized by a system of planetary electrons.
5. That the nucleus represents practically the whole of the weight of the atom, though it is very small and compact.
6. That the excess protons of the nucleus (also the planetary electrons) represent the atomic number of the element.
7. That the electrons represent the volume of the atom and are at relatively large distances from one another.
8. That the chemical properties (valence, activity, negative or positive character, and so on) of the elements are dependent on the number and arrangement of the electrons in the outer (planetary) layer.
9. That no changes in the nucleus take place except in radioactive transformation, but that all chemical changes are effected through the functions of the planetary electrons.
10. That the electrons are arranged in successive rings with the following numbers representing the maxima of electrons possible in each successive ring, beginning with the innermost: 2, 8, 18, 32, 50, 72. With the elements known at the present time, the last two shells are in-

complete. (The terms *rings* and *shells* are used interchangeably.)

Prout's and Harkins's Hypotheses. — The idea of something more fundamental than the atom was not a new one. In 1815, Prout suggested the hypothesis that all elements were made up of hydrogen combined in more or less complex aggregates and that therefore their atomic weights were all multiples of 1. This caused a great deal of controversy, but was discarded entirely about fifty years later when Stas, by some remarkably accurate analytical work, showed that the atomic weights of the elements were not whole numbers and therefore not multiples of 1. It is astonishing to note how remarkably accurate Prout's prognostications were in the light of present-day evidence, for in spite of Stas's work, chemists felt that when the atomic weights of the elements are calculated on the basis O = 16, the fact that so many of them are whole numbers, or very nearly such, could not be accidental. In fact, it was demonstrated mathematically that the chance of so many atomic weights' being practically whole numbers by accident was only one in many billions. Harkins has proposed a theory in recent times which is fundamentally the same as Prout's. He says that all elements the atomic weights of which are divisible by four are made up in the nucleus of α particles, with or without free electrons as the case may require. Thus, oxygen with atomic weight 16 has a nucleus made up of four α particles = 4 He ions, and thus gives eight excess positive charges in the nucleus. Since the atomic number (see p. 13) of O is 8, no other free electrons are necessary in the nucleus. In the case of an element like argon, with atomic weight practically 40, it is assumed that there are ten He ions making up the nucleus; but since the atomic number of A is 18, and ten He^{++} would give an atomic number of 20, it is assumed that there are two electrons in

the nucleus. This leaves an excess of eighteen positive charges in the nucleus and thus an atomic number of 18. In the cases of elements the atomic weights of which are not divisible by 4, it is assumed that the nucleus is made up of α particles, protons, and electrons. Thus, sodium, with an atomic weight of 23 and the atomic number 11, is made up of five He^{++}, three H^{+}, and two electrons. We have here thirteen excess positive charges, two of which are neutralized by the two nuclear electrons, giving an atomic number 11. Since the He^{++} has a weight equal to 4, the atomic weight of the element is $5 \times 4 + 3 = 23$.

When we consider that the He^{++} ion is believed to be made up of four H^{+} (protons) with two nuclear electrons to give the atomic number 2, it is clear that the elements according to this theory are made up fundamentally of atoms of hydrogen, which is Prout's hypothesis. (The objection that the atomic weight of He is not exactly four times that of H is met by assuming a packing effect, for the explanation of which the student is referred to a more detailed text.*)

The explanation of fractional atomic weights has been satisfactorily reached through the brilliant work of Aston and Dempster, which will be considered later on.

Chemical Action and Atomic Structure: the Langmuir, Lewis, and Kossel Hypotheses. — Since the number and arrangement of the extranuclear electrons determine the chemical activities of the elements, it would seem very important to know all about them. Unfortunately the disposition of these electrons is not settled, and a diversity of opinion exists. The physicists, represented by Niels Bohr, in order to explain certain spectral phenomena of the atom, have insisted that the electrons are in violent motion, whereas G. N. Lewis and his followers, on the other hand, to explain chemical phenomena, have proposed a static atom. Eventu-

* *S-K*, p. 531.

ally, in all probability, a hypothesis will be proposed which will embrace both satisfactorily, for both, quite evidently, have many substantiating experimental data behind them.

Since we are concerned at present only with the chemical properties of the atom, we will confine our attention to the chemist's point of view. We may consider the very inert rare gases of the atmosphere — helium, neon, argon, and the like — as standards of chemical activity, and stability of arrangement within their respective atoms, since for all practical purposes their activity is zero, and their electronic arrangement, therefore, may be considered to be the most stable. Since the helium atom is known to have two electrons outside of its nucleus, it is logical to assume that the most stable arrangement of these two electrons would be on opposite sides of the nucleus, in such a manner that a line would pass through all three centers as shown in Figure 5.

Fig. 5

Stable Electron Pair Representing Helium

The next stable and inert element occurring in order in the periodic table is neon, with ten extranuclear electrons. How are we to arrange these in a manner representing great stability? Lewis suggested that the next most stable arrangement to the pair of helium, is the octet (from whence comes the name *Octet Theory*), with eight electrons occupying the corners of a cube and inclosing the stable pair within, to make up the total of ten electrons. This might be represented as in Figure 6, though we must keep in mind that the lines are imaginary and are used only to make matters clearer.

The next inert gas is argon, with the atomic number 18, and therefore having eighteen extranuclear electrons. The

most stable configuration for it would be a pair and two octets, making three layers in all.

Having set certain standard arrangements of stability, let us now turn our attention to the more chemically active atoms and attempt to explain their behavior in terms of electrons, remembering that it is a universal tendency for

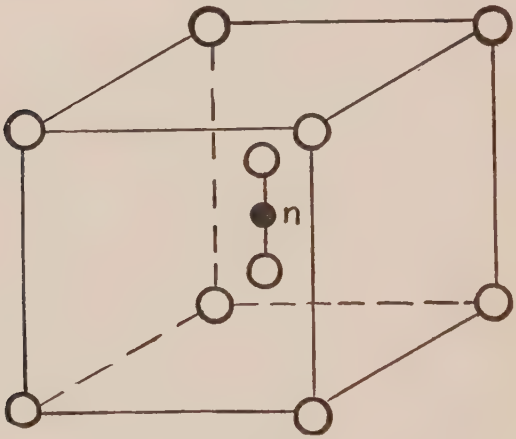


Fig. 6

Electron Structure of Neon

substances in a less stable state to approach a more stable one. In terms of electrons, then, we can say that: **All atoms tend to assume one of the more stable configurations (either a pair or an octet) in their reactions.** Consider the element lithium with the atomic number 3, and thus three planetary electrons. Two of these three complete the pair of the first shell and the third occupies one corner of the second shell cube, as shown in Figure 7.

The simplest way in which this atom could assume a stable configuration is to revert to the stable pair. This could be accomplished by the loss of the one electron in the second

shell, leaving thus a positively charged lithium atom, since the three planetary electrons were originally balanced by three protons (3^+) and the loss of one electron then leaves a proton (1^+) in excess. The marked tendency of lithium to enter the ionic state is thus simply explained. Since there is but one proton in excess, the tendency to retrieve the lost

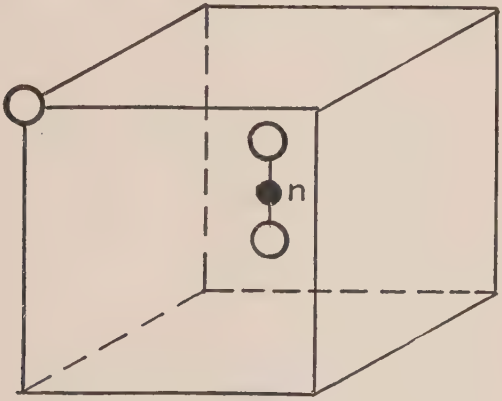


FIG. 7

DIAGRAMMATIC REPRESENTATION OF LITHIUM

electron is not very great, and we say that lithium is strongly electropositive.

The next element, beryllium, with the atomic number 4, has four planetary electrons and therefore four excess protons (4^+). This element can be assumed to have a stable pair and two corners of the second-layer cube occupied. The tendency is to give up these two second-layer electrons and revert to the helium configuration, leaving thereby two protons (2^+) which are not electrically neutralized. This forms the positive Be^{++} ion. Since there are now two protons in excess, the tendency to retrieve the lost electrons is assumed to be greater, and thus the tendency for Be to remain electropositive is not as great as for Li.

Boron, having the atomic number 5, is next. It has three electrons in the second shell. By loss of these three, the trivalent B^{+++} ion is formed, but is less electropositive than the previous two, by the same chain of reasoning.

The occurrence of carbon next introduces a new thought. Having four electrons in the second shell, it is halfway between the helium configuration with no electrons in the second shell, and the neon configuration with its full complement of eight electrons in the second shell. Should not carbon tend to go toward one structure as readily as toward the other? We should say yes, except for the belief that the pair-structure is more stable than the octet, since helium seems to be more stable than neon. Carbon, then, instead of taking up four electrons to assume the neon configuration with a valence of -4, though it can and does do this, leans more readily toward losing four electrons and assuming the helium structure with a valence of $+4$. The fact that the compounds of $+4$ carbon, such as CO_2, are more stable than the compounds of -4 carbon is taken in support of this hypothesis. It should not be thought from this that carbon forms positive and negative ions. This is explained later under "sharing" electrons.

As we pass beyond carbon, however, we approach more closely to the neon configuration. Let us first consider the element which approaches neon most closely in its structure, fluorine, with the atomic number 9, which means two electrons for the pair and seven in the second shell, as shown in Figure 8.

The nearest approach to stability here, obviously, is the assumption of one electron to complete the octet and give the neon configuration. This would give an excess of one electron and form the F^- ion, thus explaining the outstanding tendency of fluorine, which is to assume the ionic condition. The other possibility, of reverting to the helium configuration by loss of seven electrons, is not nearly so

great, since the seven positive protons left in excess would have such a large tendency to take up the electrons lost that the fluorine ion with seven positive charges would not be stable.

In a similar way, the negative trivalence of nitrogen and the divalence of oxygen may be accounted for, along with

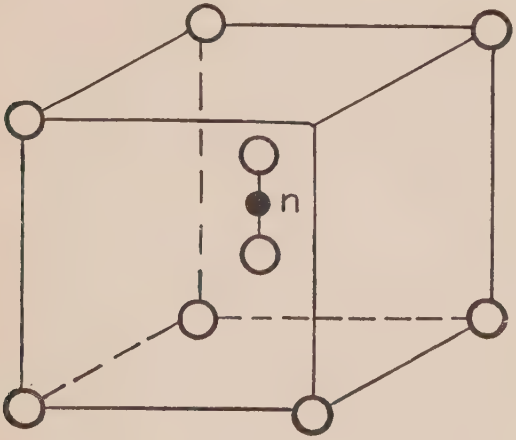


Fig. 8

Diagrammatic Representation of the Fluorine Atom

their decreasing negativity because of the increasing number of electrons to be captured and held.

The Lewis hypothesis, modified in some respects by Langmuir and Kossel, thus accounts for the valence changes in the elements as we move across the periodic table, and at the same time for their electropositive or electronegative character. We have, however, considered only the first series of elements. If we consider sodium, which has a positive valence of + 1, the same as for lithium, how are we to account for the fact that the former is more electropositive? The answer to this is believed to lie in the screen-

ing effect of the first octet. Sodium becomes an ion by losing its outer electron, since its arrangement presumably consists of a pair, an octet, and one electron in the third shell. The loss of this outer electron gives the neon configuration, but owing to the fact that the first octet is believed to exert a protective effect in preventing the excess proton of the sodium ion from recapturing its lost electron, sodium is more electropositive than lithium. In similar fashion, the lesser degree of negativity of chlorine as compared with fluorine may be explained.

How Elements Combine by Exchanging Electrons. — We have seen that the more electropositive elements tend to lose electrons and the more electronegative ones tend to gain them in order to approach more stable configurations. Here immediately a fertile possibility suggests itself. If an

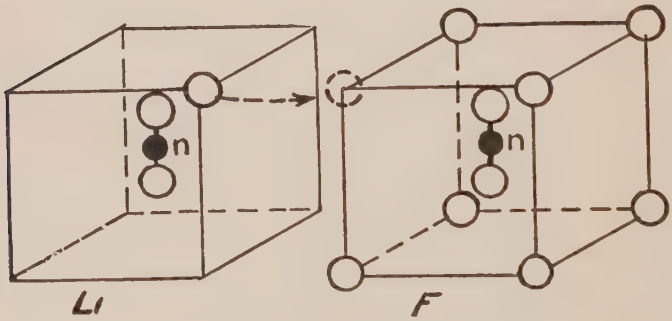


Fig. 9

Diagrammatic Representation of the Formation of Lithium Fluoride

electropositive element, say sodium, tends to lose an electron and an electronegative element, say chlorine, tends to gain one readily, should these two elements not combine vigorously, since their tendencies are complementary? We have plenty of evidence for such combinations; the most electro-

positive elements combine very readily, even violently, with the most electronegative ones, to form very stable compounds, such as lithium fluoride, sodium chloride, and potassium chloride. Let us keep well in mind the fact that such compounds are formed by an *exchange* of electrons and are really made up of separate ions. This is supported by the study of crystal structure, as was indicated previously for sodium chloride. Figure 9 is a diagrammatic representation of the combination of lithium and fluorine by exchange of an electron.

As a result of this transference, lithium has lost an electron and fallen back to the stable helium configuration, while fluorine has filled up its octet to reach the stable neon structure. The result is a very stable compound, since the two atoms each have reached a stable unit from which there is little tendency to change.

How Elements Combine by Sharing Electrons. — As was seen from their crystal structure, compounds like lithium fluoride and sodium chloride do not have their atoms actually united. As a result, when their crystals are dissolved in water, the charged atoms remain in the dissociated condition and the solution is a conductor of electricity. On the other hand, we know of many compounds which are not conductors of electricity, and it is reasonable to assume, therefore, that there is something different about the way in which their atoms are combined. Lewis postulated that, in this undissociated type of compound, instead of an exchange, there is a *sharing* of electrons. Thus, consider the combination of two atoms of fluorine to form the undissociated, stable fluorine molecule. Both atoms are electronegative, so there is no reason to assume that one will give up an electron to form an atom with one excess positive charge, while the other, gaining the electron, acquires an excess negative charge. This would mean two kinds of fluorine

atoms, and there is no reason to believe that such exist. Instead, it is assumed that each atom in complementary fashion fills its octet by sharing an electron from the octet

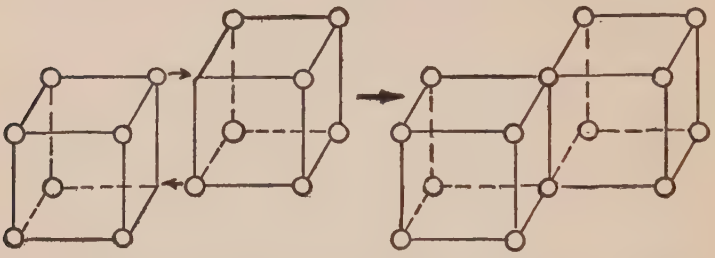


FIG. 10

DIAGRAMMATIC REPRESENTATION OF COMBINATION OF TWO ATOMS OF FLUORINE

of the other atom. The diagram in Figure 10 makes this clear (the electron pair is omitted for simplicity).

Thus by the coming together of the two atoms, the deficiency of one electron in each octet is supplied by an

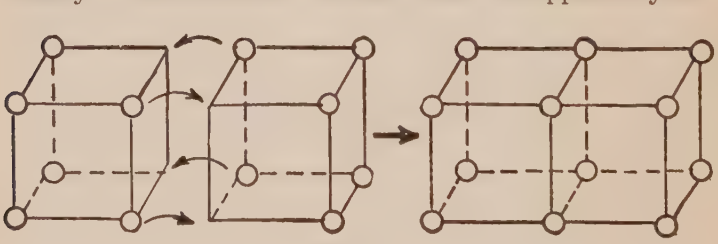


FIG. 11

DIAGRAMMATIC REPRESENTATION OF COMBINATION OF TWO ATOMS OF OXYGEN

electron from the other octet and we again have a very stable configuration. There is no transference of electrons and each atom is neutral as it was before. This is the type of combination we find in most organic compounds, which in general do not ionize.

The sharing of two electrons brings about what is called the "single bond" and in cases where two pairs of electrons are shared, the "double bond." This is the case for oxygen, for example, as shown in Figure 11.

The oxygen atom, having a deficiency of two electrons in its first octet, finds its complement in the unfilled octet of the second oxygen atom, with the resultant sharing of two pairs of electrons as shown. This formation of the "double bond" is very common in organic chemistry.

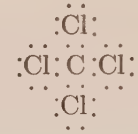
The fact that illustrations involving only atoms of one element have been used to illustrate electron-sharing should not mislead us into thinking that compounds of different elements cannot be formed in this way, for they can and are. In addition, it must be kept in mind that the lines representing the cubes are non-existent, as are the cubes themselves, and that whereas the cubes are shown in actual contact, it is probable that the position of the shared electrons is actually somewhat distorted from the position which the cube would indicate. In other words, the shared pair should probably be represented as lying *between* the two atoms.

Lewis's Method of Representation. — To facilitate drawing of the atoms and eliminate the time required to draw in the cubes, Lewis has adopted the system of representing the electrons of the outer (valence) shell by dots around the symbol for the element, arranging the dots in pairs as far as possible. Thus sodium is denoted as Na· and chlorine as $\cdot\dot{\underset{\cdot\cdot}{\mathrm{Cl}}}\cdot$ The compound of the two, sodium chloride, is given as $\mathrm{Na}^{+}\,[:\dot{\underset{\cdot\cdot}{\mathrm{Cl}}}:]^{-}$ It will be noted that the bonding pair is put nearer the chlorine symbol to show that the transference of the electron is in that direction.

Fluorine and oxygen are represented as follows:

$$:\dot{\underset{\cdot\cdot}{\mathrm{F}}}:\dot{\underset{\cdot\cdot}{\mathrm{F}}}: \qquad :\dot{\underset{\cdot\cdot}{\mathrm{O}}}::\dot{\underset{\cdot\cdot}{\mathrm{O}}}:$$

A compound like carbon tetrachloride is represented thus:



Since this compound has some ionic properties, it is assumed that the four valence electrons are transferred, at least partly, to satisfy the octets of the chlorine atoms.

Polar and Non-polar Compounds. — We have assumed that compounds which are ionized are formed by a transfer of electrons; those which are not ionized, by sharing. In so doing we have actually thought of only two extreme cases: complete dissociation in solution and complete lack of dissociation. This leaves out of consideration the many compounds which are only partly dissociated. The probability is that complete transfer and complete sharing are extreme cases and that there exist all the intermediate stages of partial transfer and partial sharing which represent the different degrees of ionization in solution.

Because compounds which are formed by transfer of electrons are like a magnet in having a negative and positive part or end, they are called *polar*. The other class of compounds, being electrically neutral, are called *non-polar*.

Electrons and Valence. — Let us consider the concept of valence in connection with electrons in a little more detail than that in which it has already been treated. At first sight, the idea of valence in terms of electrons seems quite simple; thus in the lithium atom we have a pair of electrons in addition to a single one in the second shell. These are balanced by three excess protons in the nucleus, and we say that lithium has zero valence. The lithium atom gives up its outer electron to another atom, say chlorine, and in so

doing leaves a positive charge of one proton in excess. We say that lithium now has a positive valence of one.

Consider chlorine; it has a pair in addition to seven electrons in its first octet. These are balanced by seven protons in excess in the nucleus. The chlorine receives the electron from the lithium to complete its octet. It now has an electron in excess, and we say that chlorine has a negative valence of one. Thus far we have thought of chlorine only as receiving electrons, but it has the ability to give up its own electrons in addition (at least partially). This must be assumed in order to explain the existence of compounds like the oxygen acids of chlorine, HOCl, HOClO, $HOClO_2$ and $HOClO_3$, because oxygen is assumed to be negative in all its compounds. It must, therefore, receive electrons from chlorine, the latter becoming positive as a result. In the particular instance of H^+ $:\dot{\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}}:\dot{\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}}:^-$, the oxygen has probably received an electron from the hydrogen and one from the chlorine, though the latter transfer must be much less complete, as would appear from the ionic properties of the compound. The chlorine in the ClO^- radical is, then, monovalent positive. In the same fashion, chlorine can, by loss of its electrons, be assumed to show positive valences of three, five, and seven.

Judging by what has gone before, it would seem unlikely that chlorine and other very electronegative elements would give up their electrons, but apparently they do, for the oxygen acids of chlorine can be reduced and the chlorine returned to its state in a chloride. As we shall see later, reduction is the act of returning electrons, so it is fair to assume that they have been lost.

Another fact which appears from what has been said about such compounds as hypochlorous acid and the like is that it is possible and probable that there are both polar and non-polar unions in one compound. In perchloric acid, for example, the linkage between the H and the O seems to

be polar, whereas the linkages between the Cl and the O atoms appear to be non-polar.

The question of multiple valence of an element introduces an idea of the type which we have not considered. As is well known, elements like Fe and Sn have more than one valence; iron, for example, has valences of two and three. This is explained by assuming that the valence shown in a particular instance indicates the number of electrons in the valence shell. The others are assumed to drop back into the next lower shell. This means in the case of iron that, having an atomic number 26, when its valence is two, the arrangement is two electrons in the first shell, eight in the second, fourteen in the third, and two in the outer or valence layer. When the valence is three, there are only thirteen in the third layer and three in the valence layer.

This differs from the chlorine type of multivalence, because the latter has no similar incomplete ring to which the electrons may drop back.

Isotopes. — It was previously stated that the proximity of atomic weights to whole numbers was rather remarkable. We have seen since that there is good evidence for believing that the elements are made up of unit substances. Therefore, each element, being a composite of a given number of these substances, should have a whole number representing its atomic weight. Why then does chlorine, for example, have an atomic weight of 35.46?

This question was answered by a very fine piece of work by Aston and Dempster. By taking advantage of the fact that the canal rays of the elements in gaseous form in a vacuum-tube were positively charged, and by subjecting these rays to the action of two electrically charged plates, they were able to show that the elements were *not* made up of atoms of the same mass. Instead they were found to be made up of atoms with as many as eight different atomic

weights, all close together. Thus, tin is not made up entirely of atoms with atomic weight 118.7, but a mixture of atoms, some of atomic weight 124, some 121, 119, 118, 117, and 116. The atomic weight 118.7 is only the *average* weight of the different amounts of these atoms of varying atomic weights. Since these atoms have different weights but identical chemical properties, they are called *isotopes*. All elements, of course, do not have eight isotopes. Some have only one atomic mass, as carbon and nitrogen. Others have two, three, or more.

How can we have elements with different atomic weights and yet the same chemical properties? Our electron theory answers this beautifully. If the nucleus of each has a different number of protons, the weights will vary, but if the planetary electrons are the same, the chemical properties will be identical.

SUMMARY

We have just learned that:

1. Electrons are generated in a vacuum-tube and are negatively charged particles of electricity of a weight about $\frac{1}{1867}$ that of a hydrogen atom.
2. X-rays are the same in nature as light-rays but have much shorter wave-length.
3. X-rays are due to electron bombardment and are very penetrating.
4. It is possible to determine the arrangement of atoms in crystals by means of X-ray spectra.
5. In some compounds, the atoms are not joined together to form molecules, but are separate.
6. Radioactive elements give α, β, and γ rays which correspond respectively to the canal, electron, and X-rays of the vacuum-tube.
7. Atoms are made up of a nucleus containing protons and electrons, and a planetary system of electrons.

8. The nucleus represents the weight, the planetary system the volume, of the atoms.
9. The number and arrangement of the planetary electrons determine the chemical properties of the atom.
10. The number of excess protons in the nucleus is the atomic number of the element and is more fundamental than the atomic weight, though not as useful for purposes of calculation.
11. Atomic numbers are determined from X-ray spectra.
12. Elements tend to approach stable electron arrangements in entering chemical combination. The most stable arrangement is the pair; next, the octet.
13. Atoms combine by exchange and sharing of electrons or by intermediate combinations of both processes.
14. Compounds which are ionized in solution have been formed, at least partially, by electron exchange and are called polar.
15. Compounds which do not dissociate in solution are formed by electron-sharing and are called non-polar.
16. The outer electron ring of an atom is called the *valence layer*, and by loss or gain of electrons explains the valence manifestations of the element.
17. Multivalent elements are explained by the dropping back of valence electrons into the next ring.
18. Elements are made up of isotopes. These are atoms of different mass but identical chemical properties.
19. The atomic weight is an average of the masses of the isotopes.

QUESTIONS

1. Explain what takes place in a vacuum-tube and describe the resulting rays. Do the same for radioactive elements.
2. Define the term *electron*. How can the nature of an electron's charge be shown?
3. What are X-rays? Describe three valuable uses of X-rays in scientific work.

4. Describe the structure of the atom as accepted at the present time. On what major points is there still disagreement?
5. To what men are we chiefly indebted for knowledge of the structure of the atom? Discuss the contributions of each.
6. Discuss the significance of the term *atomic number*. Whence did it originate? Who proved its significance and how?
7. What is meant by the *octet theory?* Who was its originator? Who also contributed?
8. Starting with helium, describe the first eight elements in increasing order of atomic weight, so far as their electron arrangements are concerned.
9. Tell what happens electronically when the beryllium ion is formed. Why is it less electropositive than lithium?
10. Why is sodium more electropositive than lithium?
11. Explain in terms of electrons the formation of lithium fluoride; of two atoms of hydrogen.
12. What is meant by *"sharing" electrons?* By *electron "exchange"?* To what types of compounds do these processes give rise?
13. Explain valence in terms of electrons. How is multivalence accounted for? Explain the probable electron arrangement of Mn^{++}, Mn^{+++}, Mn^{+++}, and Mn^{+++}. (Atomic number, 25.)
14. What is an isotope? How and by whom were they demonstrated? Explain their connection with atomic weights.
15. Why are all atomic weights not whole numbers? Which ones are most likely to be whole numbers and why?

CHAPTER II

DISSOCIATION

Introduction. — If we stop to classify the tests used in qualitative analysis, we find that the great majority of them depend upon the precipitation of one substance or another. The processes which lead up to the final test for an element are selective processes of solution and precipitation, each one narrowing the trail which leads to the single element. Thus, in the procedure often used for the elements Co, Ni, Mn, Zn, Fe, Cr, and Al, these are first precipitated as sulphides and hydroxides and this precipitate is treated with cold dilute HCl. This separates the sulphides of Co and Ni. Al and Zn may then be separated from the remaining three by means of boiling with NaOH and water, and then separated from each other by precipitating the hydroxide of Al. Continuing in this manner, we would see that the whole of qualitative analysis is a continuous process of solution and precipitation, with an occasional bead-test or color-test by way of exception. For accurate and intelligent analysis, then, a clear knowledge of the processes which go on in solution is indispensable.

Behavior of Electrolytes. — Let us give some consideration, then, to the phenomena which occur in solution, to facilitate our understanding of the reactions which are carried out in the laboratory. Consider in the first place liquid hydrogen chloride. It is a non-conductor of electricity and does not affect a piece of litmus-paper nor a piece of zinc dropped into it. When dissolved in benzene, in which it is reasonably soluble, the same facts hold. Its water solution,

hydrochloric acid, is quite different; it conducts electricity, turns blue litmus red, and liberates its hydrogen with zinc. Obviously, water has a marked effect on the hydrogen chloride molecule.

Similarly, if we take dry sodium chloride and endeavor to pass a current through it as a solid, the effort is fruitless, but in water solution it conducts the current easily. A mixture of dry sodium chloride and dry silver nitrate, even though it be ground a long time to produce intimate contact of the two, shows no evidence of reaction. A mixture of water solutions of the same two, however, produces an immediate precipitate of silver chloride, and the other product can, on evaporation, be shown to be sodium nitrate.

$$AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$$

Another interesting example of this kind is found in the case of copper nitrate and ammonium carbonate. If partially dehydrated copper nitrate is mixed with the above ammonium salt in the dry form and the mixture heated, a violent reaction takes place with the formation of cuprous oxide, carbon dioxide, nitrous oxide, nitrogen tetroxide and water, among other products. When these two compounds are dissolved in water and the solutions are mixed, a smooth reaction takes place with only two resulting products: a light green precipitate of copper carbonate (really basic carbonate), which may be filtered off, and ammonium nitrate. The reaction may be represented as follows:

$$(NH_4)_2CO_3 + Cu(NO_3)_2 \rightarrow CuCO_3 + 2NH_4NO_3.$$

It is obvious that the water has a marked effect on the properties of the dissolved substances. Whereas, in the case of the copper salt the reaction in the dry form caused what might be assumed to be a complete breakdown of the two compounds into their elements and recombination of these to form many products, in the case of the solutions there

seems to be a division of each compound into two groups of atoms and a simple exchange of these groups when reaction takes place, to form only two new compounds. The ability to act by double decomposition is one of the outstanding characteristics of electrolytes. It is rather remarkable, when one stops to consider, that a compound such as $K_4Fe(CN)_6$, made up of seventeen atoms, reacts when it is in solution as if it were made up of two types of units, K and $Fe(CN)_6$. Not only do electrolytes in solution behave, in double decompositions, as if they consisted of two distinct radicals, but it can be shown that they possess two independent sets of properties, one for each radical. Thus, a solution of cupric chloride owes its blue color and the precipitability of a blue hydroxide to the presence of the copper ion. These two properties among others are common to all soluble copper salts. Similarly, the solution exhibits a second set of properties attributable to the chloride ion, common to all chlorides which are soluble. These properties may be illustrated by the liberation of HCl with concentrated sulphuric acid and by the precipitation of AgCl by a soluble silver salt.

Not all compounds are affected by water in the same manner as those just mentioned. The large class of nonconductors, which are soluble in water, show none of the above properties. The examples cited above, on the other hand, are just a few arbitrary selections from the large class of conductors or electrolytes, all of which show these properties. This class embraces all the common acids, bases, and salts, the reagents of the laboratory.

It should not be thought that water is the only solvent capable of inducing the properties characteristic of electrolytes. Other solvents have the same ability, but none to such an extent as water, nor is any other solvent used as universally as is water.*

* *S-K*, pp. 329–334 and 337–339.

Boiling-Points and Freezing-Points. — Beside their characteristic chemical behavior, acids, bases, and salts show exceptional character in other properties. Thus, compared to solutions of non-electrolytes, which behave uniformly, acids, bases, and salts show abnormal boiling-points, freezing-points, and osmotic pressures. In addition to being abnormal with respect to non-electrolytes, the abnormalities with respect to each other are irregular. The explanation for both these phenomena will appear later.

We may summarize the distinguishing properties of electrolytes as follows, to facilitate their retention:

1. Characteristic chemical behavior
2. Abnormal boiling-points
3. Abnormal freezing-points
4. Abnormal osmotic pressures
5. Conductivity.*

Raoult's Law. — Before considering the meaning of *abnormal* freezing-points, boiling-points, and so on, let us briefly review the physical phenomena which underly these values, so that we may better understand them. Going back to the kinetic molecular explanation of boiling, it will be remembered that the molecules of the liquid are leaving the surface and bombarding the air-molecules in the space just above. This rain of an enormous number of molecules is, in effect, a pressure (the vapor tension of the substance). The molecules of the liquid are opposed by the pressure of the air-molecules (the atmospheric pressure). Some of the molecules of the liquid are deflected or fall back to its surface; others escape and leave the vessel, causing evaporation. This is illustrated diagrammatically in Figure 12*a*. If the temperature of the liquid is increased, the kinetic energy of the molecules is increased and they leave the surface in

* *S-K*, p. 334.

greater number and with greater rapidity, causing thus a greater pressure and more rapid evaporation. When the temperature has been sufficiently raised, the pressure of the liquid molecules will finally equal and slightly exceed the opposing pressure of the atmosphere and the liquid boils or evaporates very rapidly.

If, at this boiling temperature, the escape of some of the liquid molecules could be prevented by some means, the vapor pressure would be lowered, and the liquid would no

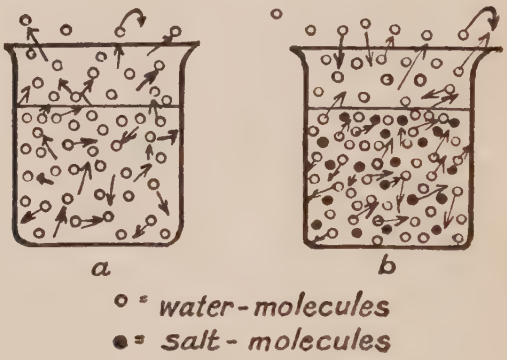


Fig. 12

longer boil at this temperature, but would require a higher one. This is exactly what is accomplished by the presence of some dissolved non-volatile material in the liquid. The molecules of the dissolved material do not go off into space as do the liquid molecules. This is evidenced by the distillation of the solution of a salt, the distillate showing none of the dissolved material. In consequence, the molecules of the dissolved material get into the way of the liquid molecules, prevent their leaving the solution so readily, and in this manner raise its boiling-point. This is illustrated in Figure 12*b*. It has been found that the hindrance is proportional to the amount of material dissolved for a given

substance. The same amounts of two different substances dissolved in the same solvent, however, do not cause equal hindrances (or depressions of the vapor pressure). If we take equal proportions of the molecular weights of two substances which are (non-volatile) non-electrolytes (say $\frac{1}{10}$ M.W. or $\frac{1}{2}$ M.W.) and dissolve them in equal volumes of the same solvent, we find that the lowering in vapor pressure is the same for both. Since like proportions of the two molecular weights contain the same number of molecules (Avogadro's Law), we may state Raoult's Law, that: **Equal numbers of molecules dissolved in like volumes of the same solvent cause equal depressions of the vapor pressure of the solvent.** The nature, size, or constitution of the molecules makes no difference.

Since equal numbers of molecules cause equal depressions of the vapor pressure, it is clear that the same increase in temperature is necessary to reach 760 mm., the vapor pressure necessary when water boils under ordinary conditions. In other words, the boiling-point is raised and raised equally for the addition of the same number of molecules in an equal volume of the solvent. Thus, a molecular weight of any non-volatile non-electrolyte dissolved in 1,000 g. of water raises the boiling-point of the latter to 100.52°. The value by which the boiling-point is increased (0.52) is called the **boiling-point constant** for water, or sometimes, the **molecular elevation constant.** This law holds in the same way for freezing-points as it does for boiling-points. A molecular weight of a non-electrolyte depresses the freezing point of 1,000 g. of water to $-1.86°$, the **molecular depression constant.** Other liquids have boiling-point and freezing-point constants, but they are numerically different from that of water.

As implied above, the effect of a dissolved material on the freezing-point of a liquid is analogous to the effect on the boiling-point. In order to coexist, ice and liquid must

have the same vapor pressure. Since at 0°, water with some substance dissolved in it must have a lower vapor pressure than ice at 0°, the water cannot coexist with it. As the temperature of ice goes down, its vapor pressure does likewise. At the temperature at which the ice has the same vapor pressure as the solution, they can coexist. In other

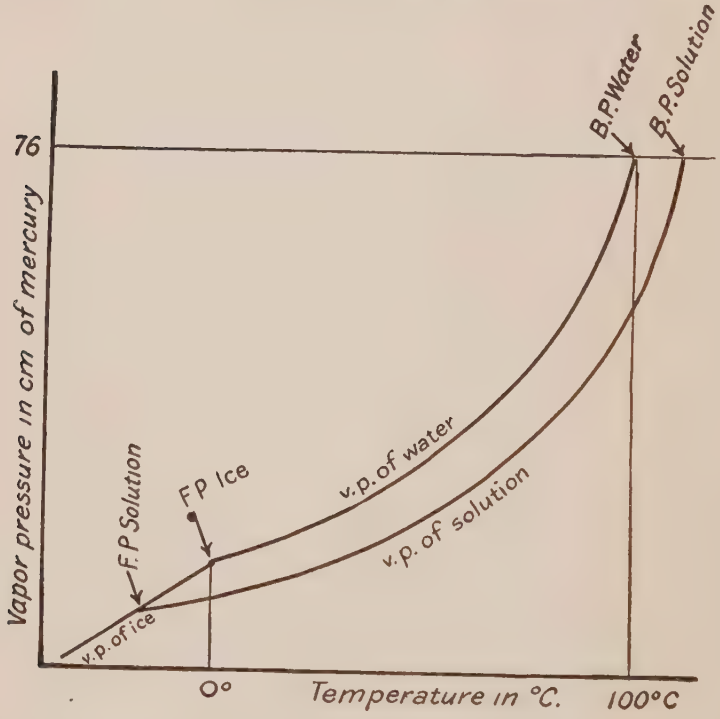


FIG. 13

words, the solution will not freeze (form ice) until this temperature is reached.

The freezing-point and boiling-point vapor pressure relationships just discussed are clarified by the accompanying diagram (Figure 13), which is self-explanatory.

It is readily seen from Raoult's Law that measurement of boiling-points, and particularly of freezing-points, offers a ready means of molecular weight determination; the latter are preferable, since they are more easily handled in the laboratory. If we take say a grams of a substance in a liter of solution and measure its freezing-point (let it be $-1.02°$), since the M.W. of any non-electrolyte in 1,000 g. of water gives a F.-P. of $-1.86°$, we may say: *

$$a : -1.02 = \text{M.W. (sought)} : -1.86.$$

$$\text{M.W.} = \frac{a \times -1.86}{-1.02}$$

Dissociation of Electrolytes. — We have seen that equal numbers of molecules of non-electrolytes have equal effects on the boiling-points and freezing-points of liquids, but we were always careful to exclude electrolytes. When we measure the molecular elevation and depression values for acids, bases, and salts, we find that they are, without exception, greater than for non-electrolytes. As before stated, the degree of their abnormality varies. To what property of acids, bases, and salts can we attribute this abnormal behavior?

To begin with, we know that a molecular weight of an electrolyte has the same number of molecules as that of a non-electrolyte. The abnormality, then, cannot arise from a greater number of *molecules* per molecular weight, or we should have a contradiction of Avogadro's Law. It is clear also that the nature, size, or constitution of the molecules seems to have no effect. The number of particles only is the controlling factor. The obvious deduction is that in some way electrolytes supply more particles per molecular weight to account for the abnormalities. Since the number of molecules per molar weight is constant, we are forced to say, in order to account for a greater number of particles,

* *S-K*, pp. 231–237.

that the molecules subdivide, i.e., dissociate. The fact that some show greater abnormalities than others simply means that some dissociate more than others.

A solution containing a molecular weight of sodium chloride (58.46 g.) in 1,000 g. of water boils at 100.97° instead of 100.52° as is the case for non-electrolytes. Similarly, its freezing-point is − 3.42° instead of − 1.86°. In both cases the value is nearly twice what it would seem it ought to be. Since a molecule of sodium chloride contains one atom of sodium and one of chlorine, the abnormal freezing-point and boiling-point values indicate that nearly every molecule is dissociated into its atoms:

$$NaCl \rightleftarrows Na + Cl.$$

If sodium chloride, which is capable of yielding only two atoms, gives freezing-point and boiling-point values almost twice normal, then a substance capable of giving three or four atoms or groups of atoms, e.g., Na_2SO_4 and $AlCl_3$ respectively, should give values which approximate three and four times the normal value. The fact that such compounds actually show values of the above mentioned order is taken as strong evidence in favor of the theory that acids, bases, and salts dissociate in solution. Of course, it must be noted that some electrolytes, such as acetic acid and ammonium hydroxide, show abnormalities which are not very great. This is explained, as previously intimated, by assuming that the dissociation is comparatively small. It will be seen presently that substances like these, which show only slight abnormalities, are at the same time poor conductors of electricity.* The degree of dissociation varies for each individual compound and may be measured by several methods, as we shall see.

Since each molecule of a compound like NaCl gives two ions, one molecular weight of substance which is 100 per cent

* *S-K*, pp. 328–338.

dissociated would give twice as many particles in solution as an entirely undissociated substance. If it were 50 per cent dissociated, there would be one and one-half times as many particles as in an undissociated substance. That is to say, assuming for the sake of convenience that there are ten molecules in solution, if one-half of them are dissociated, there will be ten ions, which, with the five undissociated molecules, makes a total of fifteen particles, or one and one-half times ten.

A substance, then, being 100 per cent dissociated, should give a freezing-point depression twice as great as an undissociated substance, and only one and one-half times as great, if 50 per cent dissociated. In other words, the increase in freezing-point depression is proportional to the degree of dissociation. Consideration of a specific case might be helpful. It was seen previously that a molecular weight of an undissociated substance such as sugar in 1,000 g. of water gives a freezing-point depression of $-1.86°$. If this were completely dissociated, it would freeze at $-3.72°$; in other words, the difference between 0 and 100 per cent dissociation is $-1.86°$.

A molecular weight (58 g.) of sodium chloride in a liter gives a freezing-point of $-3.36°$. Thus:

Freezing-point for 100% dissociation	$-3.76°$
Freezing-point for 0% dissociation	$-1.86°$
for 100% dissociation difference	$1.86°$

Freezing-point of NaCl for x dissociation	$-3.36°$
Freezing-point for 0% dissociation	$-1.86°$
for x% dissociation difference	$1.50°$

$$\% \text{ dissociation of NaCl} - x = \frac{1.50}{1.86} \times 100 = 80.64\%$$

Hence 80 per cent of all the molecules in a molar solution of sodium are dissociated.

In a similar fashion, dissociation might be measured by

determining boiling-points, or, as will be seen, osmotic pressures of solutions. The latter methods, however, particularly measuring osmotic pressure, are difficult to carry out accurately in the laboratory.

Osmotic Pressure. — Let us review briefly the kinetic explanation for osmotic pressure, so that we may better understand the activities of electrolytes and non-electrolytes in this respect. When a solution of a substance is separated from pure water by a membrane which permits the passage of the water molecules only, the water passes more readily into the solution than out of it. The reason is that the molecules of the dissolved substance hinder the passage outward of the water. Clearly, the greater the number of interfering molecules, the greater will be the hindrance. The size and nature of the molecules, as before, seems to make no difference. Since the water passes into the solution more readily than it does out, it piles up on the solution side of the membrane and thereby causes a hydrostatic pressure. As this pressure becomes greater, it slows down the incoming water molecules and speeds up the outgoing ones. The eventual effect of this is to equalize the ingoing and outgoing passage of the water molecules. The hydrostatic pressure which causes the equalization is called the *osmotic pressure.*

The dissolved molecules of the solute have nothing to do with the hydrostatic pressure itself. They act merely to hinder the passage of the water molecules. As stated before, this hindrance depends for its magnitude upon the number of solute molecules as compared to the number of water molecules — in other words, upon the amount by which the water molecules are diluted.

Another and perhaps more accurate way of viewing osmotic pressure is suggested by the experiment carried out by Sir William Ramsay. It depends upon the fact that at 300° C., palladium is quite permeable to hydrogen and im-

permeable to nitrogen. Let a mixture of the two gases, rich in nitrogen, be confined in a palladium bulb (P) by means of a manometer containing mercury to measure changes in pressure as indicated in Figure 14.

Let us assume that the levels of the mercury are at (a—a) at first. This indicates that the sum of the partial pres-

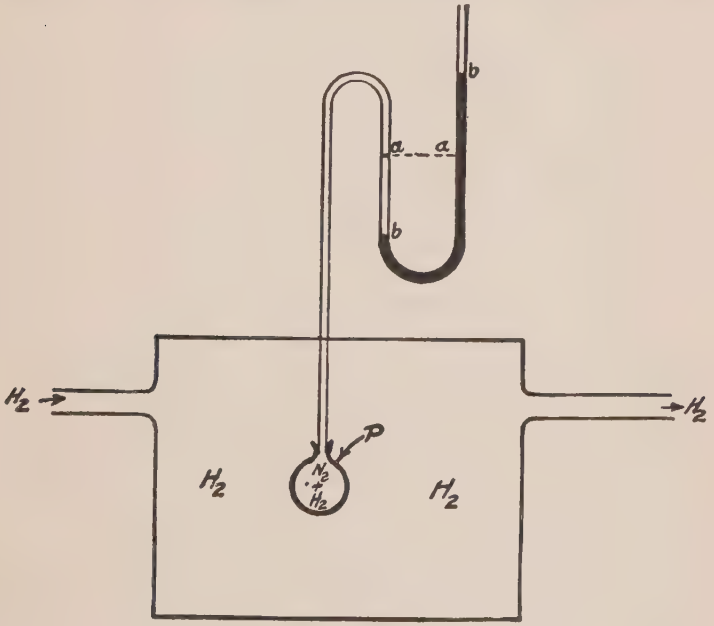


FIG. 14

sures of the hydrogen and the nitrogen together equals atmospheric pressure. If the bulb and manometer are now inserted in a box at the requisite temperature, and hydrogen is passed through at atmospheric pressure, it will pass through the walls of the palladium tube until the internal partial pressure of the hydrogen is equal to the external pressure. The total pressure within the palladium bulb is

now made up of the partial pressure of the nitrogen plus the partial pressure of the hydrogen, which is equal to atmospheric pressure. This means that the total of the two pressures has increased, as is indicated by the new manometer levels (b—b), by an amount equal to the partial pressure of the nitrogen. In the actual conduct of the experiment, results were obtained which were very close to the values demanded by theory.

Since we believe, according to the kinetic theory, that osmotic pressure and gas pressure are both results of molecular motion, it is possible that the process of osmosis is the exact analogue of the permeation of the palladium by hydrogen. In other words, having pure water on one side of a semipermeable membrane and solution on the other side, there is a condition of unstable equilibrium so far as the water molecules are concerned and they permeate the membrane until equilibrium is established.

Owing to the fact that we do not know enough about the actual processes which go on in solution, no satisfactory mechanical explanation of osmotic pressure has as yet been given. While several theories have been offered to explain osmosis, all of them are open to some criticism. The actual process seems to be a combination of several functions.

Osmotic Pressure and the Gas Laws. — A gram-molecular weight of a non-electrolyte dissolved in 1,000 g. of water gives an osmotic pressure of 23.6 atmospheres at 20°. It should be carefully noted that, although the pressure is almost the same as that given by one mole of a gas at 20°, it is not exactly the same. It is frequently stated that the laws of osmotic pressure are the same as the gas laws except for slight differences in measured values. This is the theory developed by van't Hoff, who stated that the osmotic pressure might be calculated from the equation for a perfect gas,

$$pv = RT.$$

An idea of the accuracy of this relationship can be obtained by comparing actually measured values with those calculated by van't Hoff, as shown in the following table:

TABLE I

AQUEOUS SOLUTIONS OF SUCROSE AT 20°

Osmotic pressure (calculated $pv = RT$)	*Osmotic pressure (observed)*
2.36 atm.	2.59 atm.
4.63	5.06
6.80	7.61
8.90	10.14
10.90	12.75
12.80	15.39
14.70	18.13
16.50	20.91
18.20	23.72
19.80	26.64

The values given are with increasing concentration, and it is readily seen that they digress more from the theoretical as the concentration increases. To state it in another way, we might say that in an infinitely dilute solution, making certain assumptions, the perfect gas law applies, but at ordinary concentrations there is no relationship.

Osmotic Pressure and Solutions of Electrolytes. — Since, as above stated, the osmotic pressure is proportional to the number of molecules of a substance in a given volume of water, molecular weights of different compounds dissolved in like volumes of solvent should give equal osmotic pressures and they do, if we omit electrolytes. Again, acids, bases, and salts are abnormal and give pressures which are greater than for given amounts of non-electrolytes. The degree of abnormality of a given substance is similar to its

freezing-point and boiling-point abnormality and so gives us another good piece of evidence for dissociation.*

SUMMARY

We have just learned that:

1. There are two classes of aqueous solutions. Those which do not conduct an electric current contain non-electrolytes. Those which do conduct a current contain electrolytes.
2. Acids, bases, and salts are electrolytes.
3. Water has the ability to impart to electrolytes certain characteristic chemical properties.
4. Acids, bases, and salts show abnormally low freezing-points and abnormally high boiling-points and osmotic pressures.
5. Acids, bases, and salts in aqueous solutions are dissociated to a greater or less extent into unit groups.
6. It is possible to calculate the molecular weight of non-electrolytes from freezing-point, boiling-point, and osmotic pressure data (also for electrolytes if the dissociation is known).
7. It is possible to calculate the degree of dissociation (if the molecular weight is known) of electrolytes from freezing-point, boiling-point, and osmotic pressure data.

QUESTIONS

1. Describe some of the peculiar effects of water upon salts, acids, and bases.
2. Give the kinetic molecular explanation of boiling-point elevation.
3. Think of some examples of freezing-point lowering used in everyday practice.
4. How would the freezing-point of Lake Erie compare with that of Great Salt Lake?

S-K, pp. 753–756.

5. Explain in terms of kinetic theory why molecular weights of non-electrolytes in equal volumes of solvent cause equal elevations of the boiling-point.
6. A solution of 5 g. of sugar ($C_{12}H_{22}O_{11}$) in 100 g. of water freezes at $-$ 0.272° C. What is the molecular weight of sugar?
Ans. 342.
7. The formula for glycerine is $C_3H_8O_3$. At what temperature will a solution of 5 g. in 50 g. of water freeze?
Ans. $-2.022°$ C.
8. A solution of NaCl containing 1.834 g. in 500 g. of water freezes at $-$ 0.221°. Calculate the degree of dissociation of sodium chloride. *Ans.* 89.2 per cent.
9. A solution of 5.10 g. of $BaCl_2$ in 150 g. of water boils at 100.21°. What is the degree of dissociation of $BaCl_2$?
Ans. 72.5 per cent.
10. At 18°, a $N/2$ solution of NaCl is 74.3 per cent dissociated. What would be its osmotic pressure? *Ans.* 20.80 atmos.
11. Give the kinetic explanation of osmotic pressure.
12. Describe Ramsay's experiment with nitrogen and hydrogen.
13. Discuss the connection between the gas laws and osmotic pressure.

CHAPTER III

IONIZATION

Conductivity and Ionization. — We have seen evidence in the previous chapter that the so-called electrolytes give unexpectedly high boiling-points and osmotic pressures and unexpectedly low freezing-points. In addition, we learned that they possess the rather interesting ability to react by smooth double decompositions, exchanging unit groups rather than giving a jumbled mass of all the possible compounds which the atoms present offer. We took all these facts as evidence that electrolytes are dissociated in aqueous solution into unit groups. We will now consider the clinching evidence and what is perhaps the most remarkable property of acids, bases, and salts. That is their ability in aqueous solution to conduct the electric current. Not only do they conduct the current, but their unit groups are liberated, some at the negative pole and some at the positive pole, by the passage of the current. Thus, when a solution of $CuCl_2$ is electrolyzed, metallic copper is deposited at the negative pole and gaseous chlorine is liberated at the positive.

Obviously the copper is attracted by negative electricity and chlorine by positive. From our knowledge of electrical charges, it is only reasonable to assume that the copper is positively charged and the chlorine negatively charged. We find the same type of activity for all metals and non-metallic groups (hydrogen and the ammonium radical are here considered as metals). All the metals are assumed to be positively charged and all the non-metals or non-metallic groups, such as SO_4 and NO_3, negatively.

Shall we now consider that every atom dissolved in a solution is charged, or that only a part of such atoms are charged?

The ability of different acids, bases, and salts to conduct the current helps us to answer this question. It was noted that the electrolytes which showed only slight abnormalities were poor conductors of the electric current. In general, the degree of conductance was found to be proportional to the degree of abnormality and vice versa. Since the degree of abnormality represents the amount of dissociation, and since this seemed to be directly proportional to the conductivity, it was natural to assume that only the dissociated particles were charged. The greater the dissociation, the greater therefore would be the number of charged particles or current-carriers, and therefore the greater the conductivity.

That it is reasonable to assume that the particles are electrically charged rather than not, appears from the fact that the dissociated particles must of necessity lose some of their properties. Thus, when NaCl is dissociated, if free sodium and free chlorine were liberated in the presence of water, they would both react with it, the former violently. While nothing definite is known about the effect of electrical charges upon the chemical properties of substances, it seems logical to assume that a large increase in the electrical energy content of an atom (the amount of charge will be indicated later) might easily alter its properties considerably.

Arrhenius's Theory of Electrolytic Dissociation. — Reasoning from the facts quoted, Arrhenius in 1889 proposed the theory that all acids, bases, and salts in aqueous solution are dissociated, to a greater or lesser extent, into electrically charged atoms or groups of atoms, called *ions*. These facts are indicated in the following manner:

$$NaCl \rightleftarrows Na^+ + Cl^-$$
$$Na_2SO_4 \rightleftarrows 2Na^+ + SO_4^=$$
$$AlCl_3 \rightleftarrows Al^{+++} + 3Cl^-$$
$$NaOH \rightleftarrows Na^+ + OH^-$$
$$H_2SO_4 \rightleftarrows H^+ + HSO_4^- \rightleftarrows 2H^+ + SO_4^=.$$

The above equations represent several facts which have not as yet been mentioned. They are (1) reverse arrows indicating equilibrium, (2) the number of charges associated with an atom, and (3) the two stages of dissociation of sulphuric acid. Each of these will be considered in its turn.

Ionic Equilibrium. — The fact that a solution is a conductor of electricity indicates the presence of ions. The fact that diluting this solution improves its ability to conduct indicates that more ions have been formed and therefore that molecules were originally present. The fact that evaporating the solution to dryness leaves the molecules in their original form points to the fact that molecules are formed by the union of ions. It is therefore reasonable to assume that, since there are both ions and molecules in solution, they are dissociating and recombining in a way that sets up a condition of dynamic equilibrium.

This is further indicated by the fact that a solution of a definite concentration at definite temperature gives a definite reproducible conductivity. If diluted to another measured concentration, its conductivity here is fixed and reproducible.

Faraday's Law and Ionic Charges. — If we pass an electric current through a solution of $CuCl_2$ until 35.46 g. of chlorine have been liberated, we find that 31.79 g. ($\frac{63.57}{2}$) of copper have been deposited. In other words, the quantity of electricity which will liberate one atomic weight of chlorine will deposit only one-half an atomic weight of copper. Therefore, we may say that one atomic weight of copper in solution carries twice as much charge as an atomic weight of chlorine, since it takes twice as much electricity to discharge it.

This same quantity of electricity will deposit only 9 g. ($\frac{27}{3}$) of aluminium from its compounds. Obviously, it takes three times as much electricity to deposit one atomic weight

of aluminium, and we may say therefore that each atom of aluminium is associated with three times as much electricity as each atom of chlorine. Finally, this same quantity of electricity will liberate 1 g. of hydrogen from an acid. Let us, then, take this quantity of electricity as our unit and call it a farad = 96,500 coulombs. It is the amount necessary to liberate one equivalent weight (atomic weight/valence) of an element. We may assume, then, that one gram of hydrogen in the ionic form has associated with it 96,500 coulombs of electricity. Since the number of hydrogen atoms in a molecular weight of hydrogen chloride is known with considerable accuracy, the charge on each ion can be calculated and is relatively large.

If an atom is trivalent, three farads will be required to deposit one atomic weight of it, and therefore three unit charges will be associated with it. Thus we write, Al^{+++}, Cu^{++}, Cl^{-}, $SO_4^{=}$, and so on.

The foregoing facts hold for all electrolytes and were discovered by Faraday, who stated the law that: Equal quantities of electricity liberate chemically equivalent quantities of the elements or their radicals.*

Valence and Electrons. — We have just seen that the number of charges which each atom carries in solution corresponds to its valence. From what has been said about the consitution and combination of atoms in the previous chapter, it is clear how the process of ionization takes place. Let us consider an atom of sodium and an atom of chlorine in their natural state. They are brought together and combine as a result of the sodium's giving up an electron and becoming positively charged. The chlorine receives the electron from the sodium and becomes negatively charged. The two are now combined to form a molecule of sodium chloride. This molecule is dissolved in water, which has a

* *S-K*, pp. 346–354.

peculiar ability to separate this charged atom of sodium from its oppositely charged partner and produce what we call the monovalent sodium ion and chlorine ion. The same reasoning holds for more highly charged atoms except that there is a transfer of two, three, four, or more electrons, as the case may be.

The positive valence or charge of an ion in solution, then, means nothing more than that that particular atom has given up one or more electrons to some other atom, and, as a result, has one or more protons in excess. The receivers of the electrons given up by the positive ions are the negative ions, each of which has one or more electrons in excess. In a compound consisting of two monovalent ions, the sum of all the excess positive and negative charges on the atoms which go to make up a molecular weight of that compound are equivalent to one farad of electricity, if the compound is completely dissociated.

Ionization of Polybasic Acids. — Acids having more than one hydrogen atom (this relates to inorganic acids) have the ability to ionize in stages. Thus, as before shown, H_2SO_4 ionizes first into the bisulphate (HSO_4^-) ion and the hydrogen ion (H^+), then into the sulphate ($SO_4^=$) and hydrogen ions. In the same way, phosphoric acid ionizes in three stages, thus:

$$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^- \rightleftarrows 2H^+ + HPO_4^= \rightleftarrows 3H^+ + PO_4^{\equiv}.$$

The fact that the three types of salt represented by NaH_2PO_4, Na_2HPO_4, and Na_3PO_4 are well known may be taken as proof of the existence of the three stages of ionization.

The first stage of ionization is called *primary*, the second, *secondary*, and the third, if there is such, *tertiary*. The degree of ionization is always greatest in the primary, next and much smaller in the secondary, and practically negligible in the tertiary stage, as will be indicated.

Degree of Ionization. — We have seen evidence from freezing-point, boiling-point, and conductivity data that electrolytes vary in the amount of their dissociation. Some are completely or almost completely dissociated, others only moderately so, and some are very little or practically not at all dissociated. The more an electrolyte is dissociated, the greater will be the number of ions and thus the greater the conductivity. The latter depends also on two other factors, namely, (1) the amount of charge upon each ion, and (2) the speed with which the ions move, for obviously, if an ion moves faster, it reaches the pole and is discharged more quickly, thus increasing the conductivity.

For the time being, we can assume the speeds of the ions to be constant under different conditions of dilution, and by working with equivalent concentrations eliminate the effect of varying charges on the ions. Then we may consider the conductivity as a measure of the number of ions present or the degree of dissociation of a given substance. It stands to reason, if the ions are current-carriers, that the more ions there are, the greater will be the ability of the solution to conduct a current, and that if one substance is more highly dissociated than another, it will be a better conductor of electricity.

Effect of Dilution on Degree of Dissociation. — Beside the specific ability of a substance to dissociate, there is another factor which affects the degree of dissociation, and that is the dilution. Before considering an actual case, let us take an illustration which may help us to understand the facts. The accompanying diagram (Figure 15*a*) illustrates a dance-hall divided in half by a rolling door. If a large number of couples are dancing in one-half of the hall, it is inevitable that the couples will collide with one another now and then. If the door is rolled back and the couples spread over the entire floor (as in Figure 15*b*), the number of collisions will

be reduced considerably. This is a similar situation to that of an electrolyte in solution. The dissociated ions combine to form molecules by colliding with one another. Suppose for the sake of simplicity that there are ten molecules in a certain solution. Of course, there are actually millions of molecules, but our assumption will not affect the validity of the illustration. Now let us imagine these ten molecules to be dissociating and recombining so that 60 per cent of the molecules are always in the ionic condition. Assuming

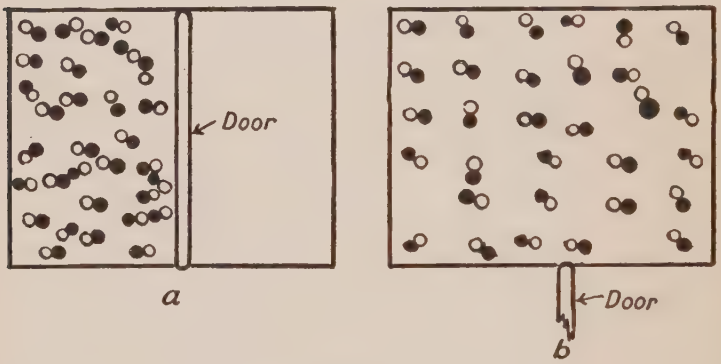


FIG. 15

the volume of our vessel to be one liter, this means that the ions are bumping into each other rapidly enough to keep 40 per cent of them constantly in the combined form. If the volume were now doubled or trebled, the ions would have a greater opportunity to wander about and so increase their distance from each other. The chances that they will come into contact as frequently under these conditions are, naturally, not as great. The *molecules* are not affected by the dilution, however, for they need not collide with one another in order to dissociate. Consequently, they will dissociate as rapidly as they did before, whereas the ions will not combine so rapidly. The net result of this is that

the number of ions increases and the number of molecules becomes less. In other words, the dissociation increases with the dilution. Since there are now more ions or current-carriers, there should be a consequent increase in the conductivity of the solution, and such is actually found to be the case.

Before developing this idea any further, let us take another analogy. Suppose it were possible to distribute a thousand people over the face of the earth and let them wander about

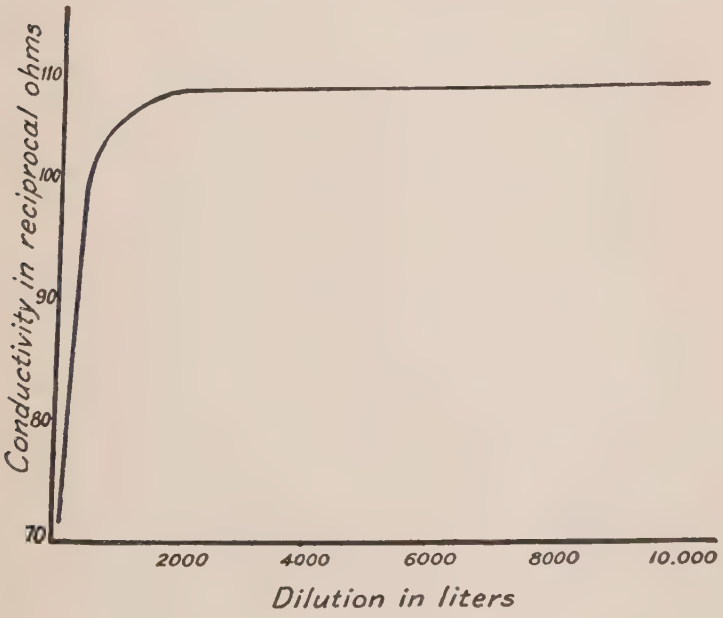


Fig. 16

at random. It is quite obvious that the possibility of any two of them meeting would be rather remote. This is similar to what happens to electrolytes at very high dilutions. Of course, as previously noted, there are many more than a

thousand ions, but they become so widely separated when dilution reaches 10,000 liters or more for a gram-molecule of a substance, that they practically never meet. Let us remember, however, that the undissociated molecules continue to dissociate as before, with the consequence that they are soon all dissociated. In other words, the substance is 100 per cent dissociated. After this condition is reached, there should be no observed increase in the conductivity regardless of how much the solution be diluted, for all the ions possible are carrying current now and the limit of conductivity has been reached. The following table for the conductivities (molar) of different acids, bases, and salts illustrates what has just been said, as does the accompanying graph (Figure 16), plotted roughly for sodium chloride. The Greek letter μ stands for molar conductivity, while its subscript represents the number of liters in which a molecular weight of the salt is dissolved. The numbers representing the conductivity are expressed in reciprocal ohms (called *mhos*) and will be explained under the head "Measurement of Degree of Ionization by Conductivity."

TABLE II

Molar Conductivities at Various Dilutions

	μ_1	μ_{10}	μ_{100}	μ_{1000}	μ_{10000}
NaCl	74	92	101	106	109
KCl	98	112	122	127	130
HCl	301	351	370	377	377
$AgNO_3$	68	94	108	113	115
$CuSO_4$	51	87	143	197	220
KOH	184	213	228	234	238
$HC_2H_3O_2$	1.3	4.7	14.5	41	107

Since in most cases the conductivity reaches its maximum value at dilutions around 10,000 liters, it is assumed that at

this concentration dissociation is complete. Theoretically, of course, ionization is not complete until the solution has been infinitely diluted. Since, for all practical purposes, ionization is complete at 10,000 liters, this is called *infinite dilution* and designated by Λ_∞.*

It is to be noted from the table that with the exception of $CuSO_4$ and $HC_2H_3O_2$, the other compounds have reached, or practically reached, their maximum values at 10,000 liters dilution.

Measurement of Degree of Ionization by Conductivity. — It has been stated that the degree to which electrolytes are dissociated may be measured by finding the degree of abnormality which the boiling-points, freezing-points and osmotic pressures of their solutions show. These methods have been used and agree closely with the values obtained by the conductivity method, though some of the discrepancies are larger than can be accounted for by experimental error. These discrepancies are taken care of in part, at least, by the theory of Debye and Hückel which will be discussed later.

The method most frequently used for the determination of degree of ionization, however, is the conductivity method, because it has certain inherent advantages not possessed by the others.

Degree of Ionization by Conductivity. — The solution whose conductivity is to be measured is placed in a cell especially designed for the purpose (Figure 17). It must be made of a glass which is resistant to the action of chemicals and contain the two electrodes (e, e) made of platinum. The water used to dissolve the salt must be extremely pure,

* Λ_∞ designates the conductivity of an *equivalent* weight of the substance at infinite dilution. Λ with any numerical subscript, i.e., Λ_{10}, indicates the number of liters in which one equivalent weight is dissolved.

because any dissolved impurities may materially affect the results obtained.

The cell is arranged in a Wheatstone bridge set-up as illustrated in the diagram (Figure 18). The known resistances (R) are adjusted so that they are approximately equal to that of the cell. Then the fine adjustment is made by

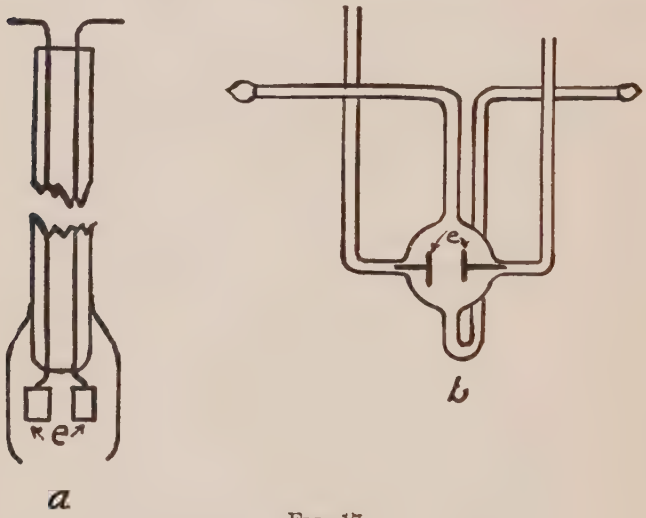


Fig. 17

Conductivity Cells

sliding the connection on the wire-bridge (ab) up and down until the hum of the induction-coil is at a minimum in the telephone receiver (T). At this point, the ratio of the resistance of the cell to the box is the same as that of one section of the bridge wire to the other. From this the resistance of the solution may be calculated in ohms, and the reciprocal of the resistance is called the *conductivity* (mhos). Since the molar strength was definitely fixed before introducing the solution into the cell, the conductivity for this

concentration is known. By increasing the dilution of the solution until the conductivity no longer increases, the value

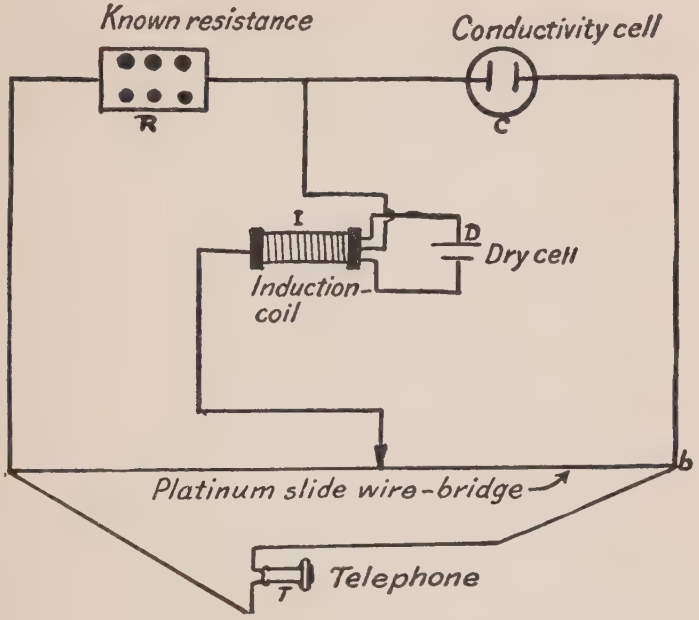


Fig. 18

Diagram of Conductivity Apparatus

for infinite dilution may be obtained. Since, from the table, Λ_∞ for HCl is 377 and Λ_{10} is 351, we may write:

$$\Lambda_{10} : \Lambda_\infty = 351 : 377,$$

or, in other words, $\frac{\Lambda_{10}}{\Lambda_\infty} = \alpha$, the degree of dissociation; and since Λ_∞ represents 100 per cent dissociation:

$$x : 100 = 351 : 377$$
$$x = 92.8\%.$$

The value of x indicates the dissociation for a M/10 solution of HCl.

We must be careful to keep in mind the fact that the conductivity at any given concentration gives no idea of the degree of ionization if the conductivity at infinite dilution is not known. Thus, the fact that at ten liters the conductivity of NaCl is only 92 is no guarantee that it is less dissociated than KCl, the conductivity of which at the same dilution is 112. Both degrees of dissociation depend on the magnitude of their respective conductivities at infinite dilution.

Conductivity of Weak Electrolytes. — It is impractical to determine the conductivity at infinite dilution for weak electrolytes, so that other means are resorted to. The details of the theory underlying this method are too extensive to enumerate here, but a brief idea may be obtained from the following considerations.

From the table of molar conductivities on page 56, it will be noted that though several of the compounds (NaCl, KCl, HCl, $AgNO_3$, and KOH) have reached their maximum conductivities at 10,000 liters, the values for these conductivities are by no means the same. When we stop to consider, we see that in each of these cases there is one molar (or equivalent) weight of the compound present and therefore the same number of molecules. Since each is considered to be completely dissociated, there must of necessity be the same number of ions. We have then the same number of ions, all equally charged, in like volumes of the same solvent. Why do they give different conductivities? Thinking back over the factors which affect the conductivity of an electrolyte, we recall that they are: the number of ions per unit volume, the charge on the ions, and *the speed with which the ions move*. The last is the only factor which has not been included in the above considerations, and it is the one which answers our problem. Since at infinite dilution the number

of positive and negative charges (the current-carriers) for an equivalent weight of any completely dissociated electrolyte is the same in all cases, we may eliminate these factors and say that the conductivity depends on the sum of the relative speeds of the two ions. This fact was discovered by Kohlrausch in studying the conductivities of various salts and is called *Kohlrausch's Law.* He noted that there was a simple relation between the values of Λ or various salts in dilute solution: thus, if we take the value of Λ for two pairs of salts with a common ion:

	K	*Na*
Cl.....	130.10	108.99
NO_3.....	126.50	105.33,

we note that the values of ($KCl - KNO_3 = 3.60$) and ($NaCl - NaNO_3 = 3.66$) are practically identical. The same is true for the values ($KCl - NaCl = 21.11$) and ($KNO_3 - NaNO_3 = 21.17$). In other words, the difference due to the two positive ions is independent of the negative ions and vice versa. The ions of an electrolyte, therefore, move independently of one another. We may say, then, that the conductivity of a salt at infinite dilution is the sum of two independent effects which Kohlrausch called the mobilities of the ions, designated respectively by U and V. Thus,

$$\Lambda_\infty = U + V.$$

Application of Kohlrausch's Law. — Let us take the case of hydrochloric acid. The relative speeds of the two ions has been measured to be H : Cl = .828 : .172. This means that of all the current carried, the H ion assumes $\frac{828}{1000}$ of the burden and the Cl ion $\frac{172}{1000}$. Since the total conductivity of HCl from the table is 377, the number which represents the H ion's ability to carry current is $.828 \times 377$ or 312 = U. This is called the *conductivity of the hydrogen ion at*

infinite dilution or its *mobility*. Similarly the value for the Cl ion would be .172 × 377 or 64.9 = V. By carrying out a similar process for a salt — like sodium acetate — which is highly ionized, we find that the conductivity of the Na ion at infinite dilution is 44.4, and of the acetate ion 33.7. Whereas we have determined the values for the individual ions using compounds which were highly dissociated and thus permitted measurements at high dilutions, we now have values which permit us to calculate the conductivity at infinite dilution of a weak electrolyte, acetic acid. Since the conductivity of the H ion is 312 = U and that of the $C_2H_3O_2$ ion, 33.7 = V, the conductivity at infinite dilution of the acid is (312 + 33.7) = 345.7.

In this manner, a table of all the ionic conductivities at infinite dilution may be constructed. Such a table is extremely helpful in calculating values for the respective compounds. The table given herewith shows the values of the conductivity at infinite dilution of a number of the more common ions, at 18° C.

TABLE III

EQUIVALENT CONDUCTIVITIES (MOBILITIES) OF IONS AT INFINITE DILUTION — 18° C.

Ion	Λ_∞	*Ion*	Λ_∞
Na	44.4	$C_2H_3O_2$	33.7
Ag	54.0	Mg/2	45.9
K	64.6	Zn/2	47.0
Cl	64.9	Ca/2	51.9
I	66.6	Ba/2	55.4
Br	67.7	Pb/2	60.8
H	312.2	$C_2O_4/2$	63.0
NH_4	64.7	$CrO_4/2$	72
NO_3	61.8	CO_3	60
OH	174	Al/3	40

To illustrate the value of this table, let us take an actual example. Oftentimes we wish to know the degree of dissociation of a salt at a given concentration and can find only its equivalent conductivity at that concentration in a reference table. Since we must know the conductivity at infinite dilution, we resort to our table to find it, by adding together the conductivities of the two ions. Thus, suppose we find that the equivalent conductivity of $N/5$ $Mg(NO_3)_2$ in the reference table is given as 82. Consulting our table above, we find that Λ_∞ is equal to (45.9 + 61.8) or 107.7. The degree of ionization then is $\frac{82}{107.7}$, or 76.2 per cent.

The degree of ionization of the various common electrolytes at the customary dilutions used in the laboratory is very important, and will be used a great deal in making explanations later. For that purpose, a table is herewith given and it is essential that the student become thoroughly familiar, not with the actual percentages, but with the approximate degree of ionization of all the common electrolytes. For example, HCl is highly ionized (about 90 per cent), $HC_2H_3O_2$ is weakly ionized (about 1 per cent), and so on.

TABLE IV

APPARENT FRACTIONS IONIZED AT 18° IN $N/10$ SOLUTION

Acids

Hydrochloric	(H^+Cl^-)	.92	Hydrofluoric	(H^+F^-)	.085
Nitric	$(H^+NO_3^-)$	.92	Acetic	$(H^+C_2H_3O_2^-)$	.013
Sulphuric	$(2H^+SO_4^=)$	.61	Carbonic	$(H^+HCO_3^-)$	.0017
Oxalic	$(H^+HC_2O_4^-)$	.50	Hydrosulphuric	(H^+HS^-)	.0007
Phosphoric	$(H^+H_2PO_4^-)$	.27	Boric	$(H^+H_2BO_3^-)$	.0001

Bases

Sodium hydroxide	(Na^+OH^-)	.91
Potassium hydroxide	(K^+OH^-)	.91
Barium hydroxide	$(Ba^{++}2OH^-)$	.77
Ammonium hydroxide	$(NH_4^+OH^-)$	.013

Salts

Potassium chloride	(K^+Cl^-)	.86
Sodium chloride	(Na^+Cl^-)	.84
Potassium fluoride	(K^+F^-)	.85
Sodium nitrate	($Na^+NO_3^-$)	.83
Silver nitrate	($Ag^+NO_3^-$)	.81
Sodium acetate	($Na^+C_2H_3O_2^-$)	.79
Sodium bicarbonate	($Na^+HCO_3^-$)	.78
Barium chloride	($Ba^{++}2Cl^-$)	.76
Silver sulphate	($2Ag^+SO_4^=$)	.70
Zinc sulphate	($Zn^{++}SO_4^=$)	.40
Copper sulphate	($Cu^{++}SO_4^=$)	.40
Mercuric chloride	($Hg^{++}2Cl^-$)	< .01
Water	< .0,000,000,002	

The above table shows the three common acids to be highly ionized, two or three others appreciably so, and the rest weak. Of the soluble bases, only ammonium hydroxide is weak. It might be mentioned in this connection that all the insoluble bases, e.g., ferric hydroxide, copper hydroxide, and zinc hydroxide, are also weak ionogens. As the table indicates, all salts, with but few exceptions (only one of which is included) are highly ionized. It is to be observed, furthermore, that water, to all practical purposes, is not ionized at all. Nevertheless, this exceedingly small ionization is a very important factor in the explanation of the activities of certain compounds, as we shall see.

Function of the Solvent in Ionization. — Up to the present, we have been considering only the electrolyte itself in the process of ionization, without thinking of any part that the solvent may take in the process. Since water is almost universally the solvent used, we have given no consideration to others, but it is a fact that other solvents permit ionization of electrolytes as well. None of them is as good a dissociating medium, however. This difference points to the fact that the nature of the solvent has something to do with

the process of ionization. The effect of the solvent may be roughly summarized as being a result of two functions: that of the dielectric strength of the solvent and that of compound formation between the solvent and the solute.

Let us consider the dielectric constant. When two equally and oppositely charged bodies are suspended at a given distance from one another in air, they attract one another with a certain amount of force. If these two charged bodies are suspended at the same distance from each other in water they still attract one another, but not with nearly the force that they do in air. We say that the water has greater dielectric strength than air and we may thus define the dielectric strength as the ability of a medium to render electrically charged bodies indifferent to one another. The force with which two like unit charges at a distance of one centimeter in air oppose one another is taken as the unit of dielectric strength. On this basis, the dielectric of water is 80. That is to say, if two unit charges repel each other with a force of one unit at a distance of one centimeter in air, they will repel one another with a force eighty times as great in water.

The connection between the dielectric constant and ionization is fairly evident. If a substance like water comes between the charged ions, it reduces their attraction for one another a great deal more than does a substance which is not such a good dielectric. In other words, it fosters dissociation by hindering association. Among the common solvents, water has by far the greatest dielectric strength and is therefore the best dissociating medium. Unfortunately, there are other factors which enter into the process of ionization, and we find that there are solvents which have higher dielectric strengths than water and yet are not such good dissociators. Thus, HCN has a dielectric constant 94, but KI is less dissociated in it than in water.

Compound Formation with the Solvent. — We shall consider only one other fact which seems to affect the extent of dissociation of electrolytes so far as the solvent is concerned, and that is the question of compound formation between the solvent and the solute. It is an outstanding fact that those compounds which are highly ionized have the ability to form hydrates with water and those which are poorly dissociated rarely do. Thus the strong acids, like HCl and HNO_3, all form hydrates which can be isolated. The weak acids, like acetic acid, if they do form hydrates, form rather unstable ones. Mercuric salts, some of which show high ionization, in these cases form hydrates; others which are not highly ionized do not form hydrates. We will consider this point again later.

The Probable Cause of Ionization. — We learned in Chapter I that when atoms unite, their electrons are involved, and that in some cases there is an exchange of electrons, while in others there is merely a sharing of electrons between two or more atoms. The former compounds we called polar because we believe that electrolytes belong to this class and as a result dissociate readily into charged ions in solution. In other words, the ions are already present in the solid molecule and only need some releasing medium like water or high temperature to cause them to dissociate. In the case of compounds where the electrons are shared, there is actual combination of the atoms and they are not present as the ions in the dry molecule. Hence they are not released when dissolved in water. These are the so-called *non-polar* compounds or unions. Thus, in the case of $NaNO_3$, the union between the sodium atom and the nitrate group is a polar one brought about by the exchange of an electron, but the unions between the nitrogen atom and the oxygen atoms are all non-polar, as otherwise we would expect to have nitrogen and oxygen ions in the solution.

Probably complete exchange of electrons and complete sharing of electrons are limiting cases, where, on the one hand, there is complete dissociation as a result, and on the other, complete lack of dissociation. Most likely there are intermediate stages of partial sharing and partial exchange which explain the varying degrees of dissociation which we encounter.

SUMMARY

We have just learned:

1. That acids, bases, and salts conduct the electric current with varying degrees of ability, in addition to showing abnormal boiling-points, freezing-points, and osmotic pressures.
2. That the particles into which electrolytes dissociate are charged, and may either be atoms or groups of atoms called ions.
3. That some have more charges than others. The number of charges corresponds to the valence and is due to an excess or deficit of electrons.
4. That equal quantities of electricity liberate chemically equivalent quantities of the ions. That 96,500 coulombs of electricity will liberate one equivalent weight of any element or ion.
5. That the degree of ionization of a given electrolyte increases with the dilution until it reaches a maximum where it is considered to be completely dissociated.
6. That from the value for complete dissociation and that for any given concentration, the per cent dissociation may be calculated.
7. That the dissociation of an electrolyte is generally measured by its resistance to the passage of a current.
8. That the conductivity at infinite dilution of weak electrolytes cannot be measured, but is obtained indirectly.

9. That the dielectric constant of a solvent probably affects the degree of ionization, and so does compound formation with the solvent.
10. That ionization is probably due to the exchange of electrons within the molecule and non-ionization is due to sharing of electrons.

QUESTIONS

1. Why do we believe that the dissociated particles of electrolytes in solution are charged? Do these charges have any influence on the properties of the atom or group of atoms?
2. Explain in detail what happens when a current is passed through a solution of an electrolyte.
3. What evidence have we for the fact that the degree of dissociation varies for different electrolytes?
4. State Arrhenius's Theory of Electrolytic Dissociation in its entirety.
5. Do the ions recombine after they are dissociated? What proof have we of this?
6. State Faraday's Laws and explain them.
7. If 1,000 coulombs of electricity were passed through a solution of copper sulphate, how much copper would be deposited? *Ans.* 0.3294 g.
8. Explain the electron theory of valence.
9. Can the degree of ionization of an individual electrolyte vary? What brings about this variation? Explain.
10. What are the factors which influence the conductivity of an electrolyte?
11. What is meant by *conductivity at infinite dilution?* How is the conductivity of any solution determined? How is conductivity at infinite dilution determined for strong electrolytes? for weak electrolytes?
12. Calculate the per cent ionization of silver nitrate at a dilution of ten liters; 100 liters. *Ans.* 81.74%; 93.79%.
13. The equivalent conductance at 18° of $CaCl_2$ is 82.8 reciprocal ohms and at infinite dilution it is 116 reciprocal ohms. What is the per cent dissociation? *Ans.* 71.5%.
14. The equivalent conductivity of $N/5$ $Cu(NO_3)_2$ is 82.4 reciprocal ohms. Calculate the degree of ionization at this concentration. *Ans.* 76.5%.

15. What is meant by the *mobility* of an ion? What effect has the mobility of the ions on the conductivity?
16. Write from memory a table of the approximate ionization values for the common acids, bases, and salts.
17. What is meant by the *dielectric constant* of a substance?
18. Explain how the dielectric value of a solvent is concerned with its ionizing power.
19. What fact besides the dielectric value of the solvent probably influences ionization? Give some illustrations to support your belief.
20. Explain, from the point of view of the electron theory, why some compounds dissociate and others do not. Explain varying degrees of dissociation on this basis.
21. Write equations for the three steps in the ionization of orthophosphoric acid.

CHAPTER IV

CHEMICAL EQUILIBRIUM

The concept of reversible changes in both physical and chemical actions is a very common one. The number of reversible chemical changes constitutes a large proportion of the total and includes almost all of the ionic reactions of analytical chemistry. A clear understanding of equilibrium is essential.

Let us therefore review briefly the ideas and characteristics of chemical equilibrium before proceeding to its application in ionization actions. Consider two substances A and B, reacting to form C and D, and that the latter are capable of reacting to form the original two. Before A and B react, their concentrations are 100 per cent and those of C and D are 0 per cent. The amounts of the former two decrease and those of the latter increase as the reaction proceeds. Kinetically this means less and less molecules of A and B, and more and more of C and D. Since the number of contacts per second of A and B decreases with their decreasing number, the reaction in this direction is slowed down. By the same token, the opposite reaction is speeded up. If one is continuously slowing down and the other speeding up, there must inevitably come a time when the two are proceeding at the same rate. Since at this point the effect of one reaction is undone as fast as it is accomplished and vice versa, neither reaction can proceed beyond the speed established at this point. A constant condition is thus maintained and the two reactions proceed without interruption. This is called the *point of equilibrium.*

Equilibrium may be reached at any concentrations of the

reactants and resultants. In other words, the concentrations at equilibrium of the opposing substances need not be equal. A moment's consideration will make this clear. Imagine that A and B, because of their inherent properties, react to form C and D readily and quickly, but that the latter react sluggishly to form A and B. Clearly, it will take much less of A and B to accomplish the same result as C and D accomplished in a given time. This means that equilibrium will be reached when the concentrations of C and D are much higher than those of A and B.

Another and non-chemical illustration may help to clarify this point. Imagine two towns on opposite sides of a bridge over which 100 people are passing in each direction per minute. There may be 20,000 people in one town and only 1,000 in the other, but so long as 100 pass in each direction per unit of time, equilibrium is maintained, that is to say, the same number of people remain on either side of the bridge.

We may, therefore, summarize the characteristics of equilibrium as follows:

1. There are two opposing tendencies which ultimately balance each other.
2. At equilibrium, the two opposing tendencies are still in full operation.
3. A change in conditions produces a corresponding change in the point of equilibrium, causing a displacement of the equilibrium in one direction or the other.

The conditions affecting equilibrium are pressure, temperature and concentration and their effects will now be considered.

Effect of Temperature and Pressure. — Since both reactions in an equilibrium cannot be equally favored by the addition of heat, it is clear that the point of equilibrium will

be shifted in one direction or the other by heating. To obey the law of the conservation of energy, one reaction must absorb and the other emit heat. It seems natural that a reaction which is trying to give off heat will oppose any effort to add heat to it, whereas the reaction which is willing to absorb heat will look upon such addition with favor. In other words, heating favors the endothermal reaction. In general the principle just stated is called *van't Hoff's Law of Mobile Equilibrium.* It may be put as follows: When the temperature of a system in equilibrium is raised, the equilibrium point is displaced in the direction which will absorb heat.

Commercially, temperature is often a very important factor in equilibrium reactions, but from an analytical standpoint, it has comparatively little application. The same applies to pressure, for this is of importance only in cases of gas reactions. Thus, in the case of hydrogen combining directly with nitrogen to form ammonia (Haber process),

$$N_2 + 3H_2 \rightleftarrows 2NH_3,$$

there are four molecules of gas on the left side and only two on the right. If the system were compressed, it would tend to go, as with all natural processes, along the lines of least resistance, which would be in this case toward the smaller volume, namely the formation of ammonia. In other words, pressure would cause a displacement of the equilibrium to the right.

Effect of Concentration. — From the standpoint of ionic reactions and equilibria, and these are the ones with which we are most concerned in the analytical field, the condition of concentration is by far the most important in influencing the equilibrium condition. Change of concentration may be classified in three ways, according as there is a mere increase or decrease in the number of molecules per unit

volume, without the formation of a gas or a precipitate, or, as is implied, there is a change in concentration due to the formation of a gas or a precipitate. Let us consider the three cases individually.

Neither a Precipitate nor a Gas Is Formed. — As in Figure 19*a*, consider a vessel containing, say, 50 c.c. of water,

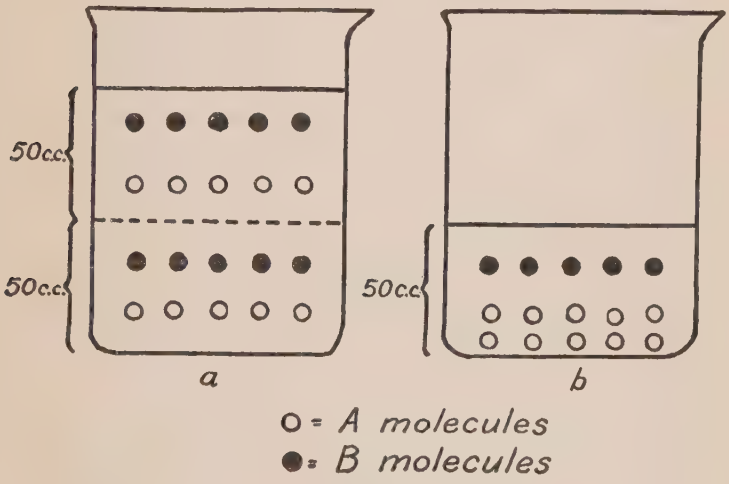


Fig. 19

in which, for the sake of simplicity, we will imagine there are five particles each of substances A and B, reacting to give C and D (not shown). Call this solution R. The particles of A and B will collide with one another a certain number of times per second to form C and D. We may write:

$$A + B \rightarrow C + D,$$

and say that this reaction has a certain speed. Let us now consider another solution, S, of the same materials and having the same number of particles in the same volume, to be

added to R. Obviously no change has taken place except to double the number of particles and the volume. To put it technically, the concentration is the same in both cases. In consequence the number of contacts between A and B particles would not be expected to increase and does not. Suppose, though, that instead of doubling the volume, we could dissolve five more particles of A in the original solution without materially increasing the volume. This condition is shown in Figure 19*b*. It is evident that now there are more opportunities for A and B to come into contact per unit of time, since they are crowded more closely together. They will thus form C and D more rapidly. The same result would obtain if instead of A, the B particles were increased without increasing the volume. If both A and B were increased without increasing the volume, the formation of C and D would be speeded up even more, and further increases of one or both would continue to speed up the reaction in the same direction. We see, then, that the speed of a reaction depends upon the number of particles *per unit volume*, but this is simply another way of expressing concentration. The latter is defined as being the mass of material per unit of volume. To put the above idea in the form in which it is usually stated: **The speed of a reaction is proportional to the molecular concentration** (see page 76) **of the reacting substance.** This is the *Law of Molecular Concentration* or, as it is often called, the *Law of Mass Action*. It will be of great importance in our explanations later on.

Effect of Gas-Formation. — If one of the products formed in a reversible reaction is a gas, this fact has a decided effect upon the point of equilibrium. Consider the familiar case of adding concentrated sulphuric acid to solid sodium chloride. As the acid is added to the salt, bubbles of hydrogen chloride are evolved. This is the laboratory method for

the preparation of the latter gas and the reaction goes practically to completion. The equation is:

(1) $NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl.$

Yet if we take a strong solution of hydrogen chloride, namely, concentrated hydrochloric acid, and add it to a concentrated solution of sodium bisulphate, a white precipitate is formed. Analysis shows this precipitate to be sodium chloride. This means that the reaction between sodium chloride and sulphuric acid is reversible:

(2) $NaHSO_4 + HCl \rightarrow H_2SO_4 + NaCl.$

In case **1**, the solid sodium chloride is dissolved to some extent in the sulphuric acid. By contact of the two kinds of molecules, the resultant products are formed. Hydrogen chloride is insoluble in concentrated sulphuric acid, however, and escapes as fast as it is formed. Since, as a result, the hydrogen chloride is almost entirely absent from the field of action, the reverse reaction can take place only to a minimum extent, so we say that reaction **1** goes to completion. In case **2**, the hydrogen chloride is in the aqueous solution and intimately mixed with the bisulphate with no chance of escape. Every molecule of each substance has opportunity to react with every molecule of the other and the reverse reaction goes on. We see, then, that the necessary requirement for reaction between substances is contact, so that if we can bring about a condition such that two of the reactants in an equilibrium cannot come into good contact with one another, the reaction will go to completion in the direction in which contact fails.

Effect of Precipitate Formation. — The precipitation of sodium chloride in the above case affords us an example of how the formation of a precipitate may affect an equilibrium. As the somewhat insoluble sodium chloride precipitates out, it settles to the bottom. Each little particle of precipitate

contains millions of molecules, which, in settling to the bottom, are just as much out of active participation in the solution as if they were outside of the container. This great reduction in the number of participating sodium chloride molecules cuts down enormously on the number of contacts between the salt and the sulphuric acid and thus retards reaction **1**, which means, as before explained, that reaction **2** goes largely toward completion.

The Law of Molecular Concentration or Mass Action. — This law has been stated in words to the effect that the velocity of a reaction is proportional to the concentration of the reacting substances. This fact may be put in the form of an algebraic equation and can frequently be applied with more facility when thus stated. A clear idea of exactly what is meant by *concentration* will be of considerable assistance in understanding the meaning and use of the equation to be derived. Concentrations are usually expressed in terms of the gram-molecular weights per liter. A *gram-molecular weight* or *molar weight* of a substance is its molecular weight in grams. Hence the molar concentration of a substance is obtained by dividing the number of grams of a substance in a liter by its molecular weight. As was previously emphasized, the big factor in equilibria is not how much of a substance is present, but how much is present in each cubic centimeter, because the concentration depends upon the closeness of the molecules to one another and not upon the number present.

Consider the reaction

$$A + B \rightarrow C + D,$$

with one mole per liter each of A and B. This reaction proceeds with definite velocity, due to the collision of molecules of A and B a certain number of times per second. The velocity is measured in terms of the number of molecules

changed or formed per second. We have the concentrations of A and B to consider, and we know that the velocity of the reaction is proportional to these two concentrations. Is it proportional to the sum of the concentrations, the product, the difference, or to what relation between them? A moment's consideration will show. Imagine the two substances A and B reacting to form C and D, but for the sake of simplicity consider that there are only two molecules of A and two of B in 10 c.c. of solution. This has no effect whatever on the validity of the deductions. A diagram to illustrate this condition is shown in Figure 20. A and B react to form C and D at a certain rate. If now the concentration of B (number of molecules per c.c.) is doubled (this might be done by dissolving some solid B and assuming there is no volume change), it is clear that A will have more opportunities per second to strike B. As a matter of fact, it will have twice as many opportunities and the reaction will go twice as fast. If now the concentration of A is also doubled, the B molecules will have twice as many opportunities to strike A. Since B has twice as many opportunities to strike A and A twice as many to strike B, the chances for contact have been increased fourfold. If the concentration of B had been trebled, leaving A at its original concentration, the opportunities for collision would have been trebled. So would the speed of the reaction. Trebling both

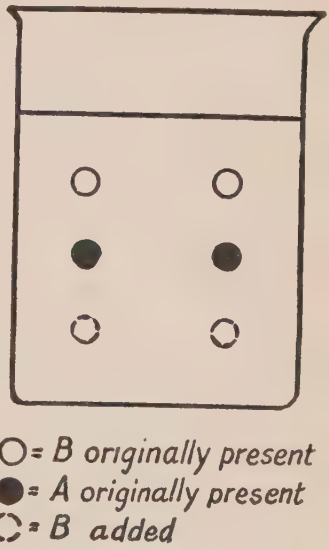


Fig. 20

concentrations would have enhanced the chances for contact of each for the other three times, in all making the opportunities for collision and the speed of the reaction nine times as great. We see then that the speed of a reaction is proportional to the **product** of the concentrations of the reacting substances.

Though the speed of a reaction is *proportional* to the product of the concentrations of the reacting substances, we cannot merely multiply these concentrations together if we wish to get an expression for the speed of a given reaction. For one thing, the speed depends on other factors beside concentrations, as already indicated. These must be taken into consideration. Furthermore, the speed of a reaction by definition is the number of molecules changed or formed per second or per unit of time. If we multiply the concentrations together, we have

C of A per c.c. $\times$ C of B per c.c., where C = concentration.

This product will obviously give a value which represents a certain number of molecules, but *not* the number of molecules changed per unit of time. Since the speed is *proportional* to the number of molecules per c.c. present, to get the change per unit of time we must introduce some factor of conversion.

An analogy may help our understanding of this. Consider two circles M and N. We know that their circumferences are proportional to their diameters D_1 and D_2 respectively, so that we may write

$$\text{circumference M} \propto \text{diameter } D_1,$$

and

$$\text{circumference N} \propto \text{diameter } D_2.$$

If, however, we wish to get a definite numerical value for the circumferences of the two circles, so that we may com-

pare them, we must introduce the proportionality constant (π). We may then write

$$\text{circumference M} = \pi D_1, \text{ and}$$
$$\text{circumference N} = \pi D_2.$$

Of course, in the case of circles, the proportionality factor (π) is the same for all. This is not true for reactions because they are not all equally influenced by temperature and the other factors which affect the speed of a reaction. The influence which each of these has varies with different reactions and different conditions. Under a given set of conditions for a given reaction, all these influences may be considered constant and summarized in the form of a constant (k). This constant is characteristic of a *given reaction* under *given conditions only*. It includes all the influences but that of concentration, because the effect of the latter is the one most easily measured. For a reaction

$$A + B \rightarrow C + D$$

then, we may write an expression for the speed in the forward direction, as follows:

$$[A]^* \times [B] \times k = \underset{\rightarrow}{S}.$$

Limitations of the Concentration Law: Activity. — In using the kinetic molecular theory to arrive at the conclusions stated in the law of molecular concentration, no consideration was given to the nature of the interacting substances nor to their possible effects upon one another, other than to react to form new substances. It is a well-known fact that any two bodies have an attraction for each other which is inversely proportional to the square root of the distance between them; that is to say, their attraction

* The square brackets [] are used to indicate concentration, thus: concentration of A = [A].

diminishes as the distance increases. Thus, if two molecules pass close to one another in solution, their respective velocities would be somewhat affected by mutual attraction as they approach one another. In a dilute solution, where the space between the molecules is exceedingly large, these attractive disturbances are relatively minute and negligible. When the solution becomes concentrated, however, the molecules are much closer to one another, with the result that the attractive forces begin to have a decided effect upon the speed of the molecules. This is manifested in the speed of the reaction. In other words, the speed of a reaction is not strictly proportional to the concentration of the reacting substances, particularly when the concentrations become fairly large.

Since the speed of a reaction depends upon the speed of the reacting molecules, and this latter speed is only some fraction of what it would be if there were no attractive force, let us say that an unhampered molecule has an activity A, but when it is under the influence of attractive forces, it has an activity of only a. The ratio of these two values a/A is called the *activity coefficient* (f). It varies with the concentration. In a very dilute solution where the attractive forces are negligible, a is very nearly equal to A and f, the activity coefficient, is equal to 1, so the concentration law holds. As the concentration increases, a begins to vary appreciably from unity and the mass law does not describe the facts. In conclusion, it may assist us to think of A as the true concentration of a substance under consideration and of a as the apparent concentration.

In view of the fact that the concentration law is of the most fundamental importance in all analytical work, it would seem essential that we have a very definite knowledge of the activity coefficient in order successfully to apply the law in our work. It must be remembered, however, that whereas the concentration law does not hold in a mathe-

matically quantitative way because of activity considerations, it still holds very well in an approximate way. Since we are interested in explaining things only in a qualitative way and not in exact numerical fashion, we need not be troubled by the above-mentioned deviations. For these reasons, in the derivations which follow, no attempt will be made to consider activities.

Derivation of the Mass-Action Equation. — Let us consider again the general equation

$$A + B \rightleftarrows C + D$$

at a certain temperature. Then we may say, using S_1 for the velocity, and [A] and [B] respectively for the concentrations (molar) of A and B,

$$[A] \times [B] \times k_1 = S_1,$$

where k_1 is the aforementioned proportionality constant.

Similarly, if the above reaction is a reversible reaction, the reverse reaction will have a constant k_2, and under a definite set of conditions, a certain velocity — call it S_2. We may write

$$[C] \times [D] \times k_2 = S_2.$$

This gives us a definite expression for the velocity of either reaction at a given moment. Let us consider only the time when equilibrium is reached, or, as stated, when the velocities of the opposing reactions are equal. At this point, $S_1 = S_2$, so we may say:

$$[A] \times [B] \times k_1 = [C] \times [D] \times k_2$$

or

$$\frac{[C] \times [D]}{[A] \times [B]} = \frac{k_1}{k_2}.$$

But since k_1 and k_2 are constants, and a constant divided by a constant gives another constant, we have

$$\frac{[C] \times [D]}{[A] \times [B]} = K_{T^\circ},^*$$

where T° designates a given temperature.

The case just considered is of a simple type, with only one molecule each of the reactants and resultants. The relations are not as simple in the following reaction:

$$A + 2B \rightarrow C + D.$$

This case is better understood by considering that there are three substances, A, B, and Q, reacting to give C + D. This would give

$$\frac{[C] \times [D]}{[A] \times [B] \times [Q]} = K.$$

Now, suppose an identical amount of B to be substituted for the amount of Q present. We may then substitute [B] for [Q] and the above expression becomes

$$\frac{[C] \times [D]}{[A] \times [B]^2} = K.$$

The same reasoning would apply if there were three molecules of B taking part in the reaction instead of two, or in general, **that power of the concentration is used which expresses the number of molecules of a substance participating in the reaction.** As an example of a more complex case, take the reaction between ferric chloride and ammonium thiocyanate, which is expressed by the equation:

$$FeCl_3 + 3NH_4CNS \rightleftarrows Fe(CNS)_3 + 3\ NH_4Cl.$$

* In what follows, T° will be omitted from K_{T°. Unless otherwise indicated, the letter K will indicate the value of the particular constant at one temperature only.

The mass-action equation would be:

$$\frac{[Fe(CNS)_3] \times [NH_4Cl]^3}{[FeCl_3] \times [NH_4CNS]^3} = K.$$

The equation for the Law of Mass Action of the type just developed is a general one and applies to any *equilibrium*, regardless of the number of reactants and resultants, although there is an important class of exceptions which will be treated later (strong electrolytes).

Application of the Equation. — The method of application of the equation may be seen by considering first, the general case of $A + B \rightarrow C + D$ and then the specific one of ferric chloride and ammonium thiocyanate.

When two substances A and B, in certain concentrations, react to give C and D, we may write the equation:

$$\frac{[C] \times [D]}{[A] \times [B]} = K.$$

Now let us suppose that the concentration of C [C] be increased by the addition of some solid C to the solution which contains the four reacting materials. This may be represented (for an instant) as follows:

$$\frac{[C]^* \times [D]}{[A] \times [B]} > K.$$

Obviously, the value of the product of the concentrations of $[C] \times [D]$ divided by $[A] \times [B]$ is now momentarily greater than the constant K. If our law is valid, this condition cannot continue to exist. A change must take place to bring back the value of the equation to K. This may happen in three ways:

1. The value of the numerator may become smaller.
2. The value of the denominator may become larger.

* The enlarged [C] indicates a larger concentration than was originally present.

3. The value of the numerator may become smaller as the denominator becomes larger.

Inspection shows that the third is the possibility which actually occurs. If [C] or [D] were to become smaller (in order to make [C] × [D] smaller) either could become so only by reacting with the other. Consequently both become smaller. But when C and D react with one another, according to the equation, they can form only A and B, so if [C] × [D] is to become smaller, then [A] × [B] must become larger. Stating it the other way around, if [A] or [B] is to become larger, it must be at the expense of [C] and [D], but its partner must become larger at the same time. *Let* x *represent the amount by which* [C] *and* [D] *are diminished.* The equation might now be written:

$$\frac{([C] - x)([D] - x)}{([A] + x)([B] + x)} = K.$$

The net result is that the value of the constant is reached again, but a new point of equilibrium is established. Obviously, too, the concentration values of the reacting substances at the new point of equilibrium are different from the original values.

The application to the case of ferric chloride and ammonium thiocyanate is now almost self-evident. Let the equation at a certain point of equilibrium be:

$$\frac{[Fe(CNS)_3] \times [NH_4Cl]^3}{[FeCl_3] \times [NH_4CNS]^3} = K.$$

If now the concentration of the ferric chloride or of the ammonium thiocyanate, or of both, be increased, the opportunities for the collision of the molecules (omitting ionic considerations for the sake of simplicity) will be increased. As a result, more ferric thiocyanate and ammonium chloride will be formed. Since the ferric thiocyanate is red in color, the solution will become a darker red. In terms of the

equation, the value of the constant will not be reached by the increase of $[FeCl_3]$ or $[NH_4CNS]$ or both. They must become smaller to reëstablish the value of the constant. They can do so only by forming $Fe(CNS)_3$ and NH_4Cl, so increasing $[Fe(CNS)_3]$ and $[NH_4Cl]$. If the concentration of the ammonium chloride ($[NH_4Cl]$) is increased instead of that of ferric chloride or ammonium thiocyanate (the reverse process), $[FeCl_3]$ and $[NH_4CNS]$ become larger at the expense of $[Fe(CNS)_3]$ and $[NH_4CNS]$, and the color becomes lighter.

A simple numerical illustration may help to make these relationships clearer. Let us suppose, in the case under consideration, that the four concentration values of the reacting substances can be measured after equilibrium is established. Let these equilibrium concentrations in gram-molecules per liter at 25° be as follows:

$$[FeCl_3] = 0.5 \qquad [Fe(CNS)_3] = 0.8$$
$$[NH_4CNS] = 0.7 \qquad [NH_4Cl] = 1.0.$$

By substituting in the equation, we can calculate the value of the constant as follows:

$$\frac{(0.8) \times (1.0)^3}{(0.5) \times (0.7)^3} = 4.67.$$

If we bring the substances together in any other concentrations than the above, the reaction will go one way or the other until the concentrations are adjusted to such values as will give $K = 4.67$ again.

Ionic Equilibrium. — As before stated, the Law of Mass Action applies to any case of substances in equilibrium. It applies, therefore, to all electrolytes where there is an ionic equilibrium between the ions and the un-ionized molecules. This is the type of reaction with which we deal almost exclusively in analytical work. The case is somewhat simplified because in general there are only three factors involved:

the concentrations of the two ions and the un-ionized portion. For an electrolyte AB, we have

$$AB \rightleftarrows A^+ + B^-.$$

The ionic equation is

$$\frac{[AB]}{[A^+] \times [B^-]} = K,$$

or better,

$$\frac{[A^+] \times [B^-]}{[AB]} = K.$$

The latter is the more generally used expression and is equally as applicable as the former. The only difference lies in the value of the constant, which in one case is merely the reciprocal of the other. In the case of ionic equilibria, the constant is generally termed the *ionization constant.*

A brief consideration of the numerical relationships involved in evaluating the ionization constant will help to establish its significance. Consider the substance AB (at a given temperature) to be present to the extent of one mole per liter in a solution, and to be ionized to the extent of 20 per cent. The concentration of the un-ionized portion is then 0.8 (80 per cent). The remaining 0.2 gram-molecules are each dissociated into the two ions A^+ and B^-, so the **gram-molecular concentrations** of each of these is 0.2. These values, inserted into the equation above, give

$$\frac{(0.2) \times (0.2)}{(0.8)} = K_T = 0.05.$$

To illustrate how these values may be used, let us consider a case the validity of which we have already established in another way, namely, the effect of dilution on the degree of ionization. Assume that to the above liter of electrolyte AB, a liter of water is added. The result is that each ion and molecule has just one-half its former concentration value or

$$\frac{(0.1) \times (0.1)}{(0.4)} = (0.025) = K.$$

The numerical value of K is now only one-half its original value. According to our law, the value of the constant must remain constant at 0.05. To fulfil this requirement, the numerator must increase and the denominator decrease until the original value (0.05) is restored. This change is affected by $[A^+]$ and $[B^-]$ becoming larger (if one becomes larger, the other must). The only way in which $[A^+]$ and $[B^-]$ can become larger is at the expense of [AB]. This in turn means that the dissociation increases with the dilution. The same conclusion was reached from the kinetic viewpoint, previously considered.

In order to convey some idea of the actual magnitude of the ionization constant, K, the following table gives actually measured values at different concentrations for the degree of ionization of acetic acid at 18°, along with the value of the constant at each concentration. The molal concentration of the ions is obtained by multiplying the fraction ionized by the number of moles present. The fraction ionized is obtained, obviously, by dividing the per cent ionization by 100.

TABLE V

	Total mol. conc. of acid	*Per cent ionized*	*Mol. conc.* $([A^+]=[B^-])$ *of* H^+ *and* $C_2H_3O_2^-$	*Mol. conc.* $([AB])$ *of* $HC_2H_3O_2$
(1)	1.00 (60 g./liter)	0.41%	0.0041	1.0 − .0041 = .9959
(2)	0.10	1.30%	0.0013	0.10 − .0013 = .0987
(3)	0.01	4.07%	0.000407	0.01 − .000407 = .009593

The equation for acetic acid would be

$$\frac{[H^+] \times [C_2H_3O_2^-]}{[HC_2H_3O_2]} = K_{18°}.$$

Substituting the values from the above table:

(1) $$\frac{0.0041 \times 0.0041}{0.9959} = 0.0000169$$

(2) $$\frac{0.0013 \times 0.0013}{0.0987} = 0.0000171$$

(3) $$\frac{0.000407 \times 0.000407}{0.009593} = 0.0000172.$$

Although in case **3** the acetic acid is 100 times more dilute and ten times more highly ionized than the first, the constant is practically the same. It is to be noted that dilute solutions of a weak electrolyte were selected because, as was said before, the law does not hold mathematically for concentrated solutions and strong electrolytes.

The Question of Molecular Concentration. — The question of the gram-molecular concentration of the ions sometimes causes confusion to students. For example, suppose we have a gram-molecular weight of a substance, AB, the molecular weight of which is 60. At a given temperature it is 50 per cent dissociated. Let the atomic weight of A be 40 and that of B 20, for simplicity's sake. On the basis of what has just gone before, we would say that the concentration of the unionized portion is 0.5 and that for each of the ions it is 0.5. How are we justified in saying that the molecular concentration of each of the ions is 0.5? Of the 60 g. of AB present, 30 are dissociated and of these 30, 20 g. are A and 10 g. are B. Yet we say that the molecular concentrations are the same.

It is to be remembered that the opportunity for collision does not depend upon the weight of the molecules but upon the number of them present per c.c. So in the case just cited, even though there is a *greater weight* of A ions than B ions present, the number of each is the same, for when AB dissociates into A ions and B ions, there is one B ion

and one A ion for each molecule that dissociates. Consequently, B is just as effective in bringing about collisions as A. The speed of the reaction depends upon the number of collisions per unit of time. Hence, the concentration of B should be considered to be the same as that of A. We might view this in another way by saying that, since there are 20 g. of A and 10 g. of B, and since their respective atomic weights are 40 and 20, their concentrations are respectively $\frac{20}{40}$ and $\frac{10}{20}$. We thus arrive at the same conclusion.

Limits of Applicability of the Mass-Action Law. — It is evident from the value of K for different concentrations of acetic acid that the mass-action equation may be applied with considerable accuracy. The same is true for other weak electrolytes in dilute solutions. As the concentration increases, however, the value of K diverges more and more from its constant value. This is clearly indicated in the following table for the dissociation constant of acetic acid at 25°. The value of K is given at various dilutions, where V is the number of liters containing 1 mol (60 g.) of acetic acid:

TABLE VI

V	$K \times 10^5$	V	$K \times 10^5$
1,000	1.84	15	1.84
500	1.84	7	1.81
250	1.84	4	1.76
60	1.85	2	1.65
30	1.85	1	1.65

The obvious lack of constancy at higher concentrations might have been anticipated from what has been said of activity. In spite of the apparent divergencies, however, the values over a wide range of concentrations are not ex-

tremely great, and in a qualitative way they are quite satisfactory.

In the case of strong electrolytes, we might correctly anticipate that, owing to high dissociation, the manifestation of attractive forces between the great number of positively and negatively charged ions would be even greater. Experiments show that the values of K, even over moderate ranges of concentration, are in no sense constant. The following table gives the values of K for a strong electrolyte, potassium chloride at 18° C.:

TABLE VII

V	$K \times 10^3$	V	$K \times 10^3$
10,000	15.4	50	222.1
5,000	22.3	20	364.2
2,000	35.2	10	540.5
1,000	48.5	5	815.4
500	68.1	2	1434.
200	108.4	1	2350.
100	154.2		

It is quite evident that, at ordinary ranges of concentration used in the laboratory, the Law of Mass Action does not hold at all.

Many attempts have been made to explain the anomalous character of strong electrolytes. The mass-action equation has been modified in many ways to meet the variance. All of them were purely empirical and none was satisfactory, particularly as there was no real theoretical basis for the majority of them.

Modern Theories of Dissociation. — A. A. Noyes in 1908 postulated that strong electrolytes were, at least potentially, completely dissociated. X-ray work on crystal structures

indicated that a crystal of solid sodium chloride or fluoride contained *no molecules at all*, but that the elements, even in the solid form, were present as ions. As a result, Debye and Hückel have proposed a theory of complete dissociation. They state that strong electrolytes are almost entirely dissociated and that the divergencies from the mass-action principle are due to electric forces between the ions. By means of equations derived by Debye and Hückel, it is possible to calculate what the "activity" of an ion is, and therefore its "apparent" concentration. For dilute solutions, the above assumptions have been tested and found to be in excellent agreement with the facts. Unfortunately, when concentrated solutions of strong electrolytes come into play, the above equations do not hold. Evidently other factors must be taken into consideration.

There must be combination of one sort or another between the ions and the solvent. It can hardly be a coincidence that highly ionized acids, bases, and salts all have the ability to form hydrates, whereas the weakly ionized ones do not have this ability. It is rather striking that the highly ionized acids, H_2SO_4, HCl, and HNO_3, all form hydrates, whereas not a single example of a stable hydrate can be found among the many weak acids. It is clear that if there is hydrate formation between the solvent and the ions, concentration changes must take place, since the solvent is consumed in hydrating the ions. These concentration changes unquestionably affect the validity of our mass-action calculations.

Another factor which must be given consideration is the volume occupied by the ions themselves. In dilute solutions the volume is negligible. When the concentrations increase, the volume of the former becomes appreciable and must be considered. We can only await further developments along such lines as the Debye-Hückel theory for answers to these problems.

Meanwhile, let us not lose sight of the fact that, although we use strong electrolytes in analytical work, the solutions in which we make our final tests are seldom concentrated. Hence the assumptions of Arrhenius, though quantitatively inaccurate, serve as an excellent and adequate basis for the explanations we wish to make.*

SUMMARY

We have just learned:

1. That in an equilibrium there are two opposing reactions going on at equal rates of speed so that apparently nothing is being accomplished.
2. That a change in the conditions governing the equilibrium brings about a change in the point of equilibrium, so that theoretically equilibrium may be reached at an infinite number of points for the same set of reactants.
3. That the factors which affect the point of equilibrium are pressure, temperature, and concentration.
4. That the speed of a reaction is proportional to the product of the molecular concentrations of the reactants (Law of Mass Action).
5. That the concentrations at equilibrium may be expressed in the form of an equation which helps us to predict what will happen when a given change in concentration is brought about.
6. That the Law of Molecular Concentrations (or Mass Action) does not hold quantitatively for more concentrated solutions.
7. That the above law applies to ionic equilibrium.
8. That the product of the concentrations of the ions divided by the concentration of the un-ionized molecule is a constant for any one temperature. This is called the **equilibrium constant** for that substance at that temperature.

* *S-K*, pp. 812–814.

9. That electrolytes may be completely dissociated, but do not manifest their complete dissociation because of electric forces exerted by the ions on one another.
10. That in dilute solutions, the apparent concentration may be expressed by multiplying the real concentration by an "activity coefficient" (f).
11. That in concentrated solutions the concept of activity does not seem to explain all the facts.
12. That even though the Law of Molecular Concentration may not hold quantitatively, its use in qualitative analysis is not at all impaired.

QUESTIONS

1. Develop the equilibrium equation $\frac{[C] \times [D]}{[A] \times [B]^2} = K$.
2. Make a list of five reversible reactions you learned in general chemistry. Write out these equations with a discussion of what conditions will cause each one to go to the left ($\leftarrow$) or to the right ($\rightarrow$).
3. Discuss all the ways in which a reversible reaction in equilibrium may be disturbed.
4. How is the value of a constant for a chemical equilibrium affected by a change in concentration of the reacting substances?
5. What factors influence the velocity of a chemical change? Which ones of these are under the control of the experimenter?
6. Name and describe two general methods of causing an ionic equilibrium to go toward completion.
7. Suppose two substances, A and B, react reversibly with one another under constant temperature. What happens to their concentrations and to the rate of reaction, from the instant of mixing?
8. Work out the quantitative effect of adding to a normal solution of acetic acid an equivalent amount of sodium acetate. (The sodium acetate is 0.53 ionized.) *Ans.* $[H^+] = .0_434$.
9. What is the concentration of the hydrogen ion and the acetate ion in a 0.1N acetic acid solution to which a normal solution of hydrochloric acid has been added in equal quantity?
   Ans. $[H^+] = .9202$; $[Ac^-] = .0_315$.

10. When silver chloride is formed by the interaction of solutions of silver nitrate and sodium chloride, why does the reaction apparently go to completion?
11. Mercuric oxide can be formed by heating mercury in the air. It can be decomposed into mercury and oxygen by heating. Explain.
12. Why can magnetic oxide of iron be reduced completely by a stream of hydrogen? Why can the reverse reaction of oxidizing iron by steam be also completely brought about?
13. From the table on page 63, calculate the ionization constants for the primary ionization of the following acids: carbonic, acetic, and phosphoric.

    Ans. $K_{H_2CO_3} = .0_63$; $K_{HC_2H_3O_2} = .0_418$; $K_{H_3PO_4} = .01$.
14. What is the molar concentration of the acetate ion in $N/10$ acetic acid? of the chloride ion in $N/10$ hydrochloric acid? of the sulphate ion in $N/10$ sulphuric acid?

    Ans. $(HC_2H_3O_2)[H^+] = .00134$; $(HCl)[H^+] = .092$; $(H_2SO_4)[H^+] = .0305$.
15. The solubility of $Mg(OH)_2$ is 0.00875 g. per liter at 20°. Assuming that it is completely dissociated at this concentration, calculate the concentration of the Mg and the OH^- ions.

    Ans. $[Mg^{++}] = .0_315$; $[OH^-] = .0_33$.
16. What is the concentration of the OH^- in a $N/10$ solution of NH_4OH? Calculate the strength of an NaOH solution that would be necessary to supply the same OH^- concentration, assuming that the NaOH is completely ionized at this strength.

    Ans. $(NH_4OH)[OH^-] = .00134$; $(NaOH) = .00134N$.
17. Water dissolves 0.001433 g. of AgCl at 20°. Assuming complete ionization, what is the concentration of the Ag ion in a saturated solution of AgCl? *Ans.* $[Ag^+] = .0_41$.

CHAPTER V

HETEROGENEOUS EQUILIBRIUM AND THE SOLUBILITY PRODUCT PRINCIPLE

Heterogeneous and Physical Equilibrium. — In the cases of equilibrium previously considered, the reacting materials have practically all been either in solution or in the gaseous form. These are called cases of homogeneous equilibrium because the concentrations of the materials are the same in all parts of the mixture.

Many operations in qualitative analysis have to do with the formation and dissolving of precipitates. In such cases, we have equilibrium between the particles of a substance in the dissolved and solid states, if the solution is saturated. The materials are not mixed in a uniform manner with one another. This is called **heterogeneous equilibrium.**

In an equilibrium between a saturated solution of a substance and the solid lying at the bottom of the vessel, it is easy to define the concentration of the dissolved portion because the solubility of the substance is known. It is not difficult, either, to imagine how all the dissolved particles of the substance are available for reaction. It is a different matter in the case of a solid. Only the molecules at the surface of the solid are available for reaction. Only these can have any effect upon the reaction. These available molecules are called the *active mass* and may be considered constant for qualitative purposes. Actually, this is not strictly true.

The relationships which hold in the case of heterogeneous equilibria are analogous to those for homogeneous equilibria. Take, for example, a solid, S, dissolving in a liquid, giving

dissolved molecules until equilibrium is established. This occurs when the number of molecules leaving the solid and going into solution per second is equal to the number being deposited on the solid from the solution; in other words, when the solution is saturated. The speed of the dissolving reaction will be proportional to the concentration of the molecules in the solid state, say [s]. Call the speed in this direction S_1. The speed (call it S_2) of the opposing reaction will be proportional to the concentration of the dissolved (but un-ionized) molecules [m]. Let K_1 and K_2 be the proportionality constants respectively, for the two reactions; then:

$$(1) \quad [s] \times K_1 = S_1;$$

$$(2) \quad [m] \times K_2 = S_2.$$

At equilibrium $S_1 = S_2$, therefore:

$$(3) \quad [s] \times K_1 = [m] \times K_2,$$

or

$$(4) \quad \frac{[s]}{[m]} = \frac{K_2}{K_1} = K$$

This is an expression very similar to the one just derived for the Law of Mass Action. To state it in words, we may say that: **At a given temperature, the ratio of the concentrations of the molecules in the dissolved (but un-ionized) state to those in the solid state is a constant when equilibrium is established.**

The Solubility Product Principle. — Equations have now been developed which apply to each of the equilibria which exist when we have a saturated solution of an electrolyte, namely an equation for the equilibrium between the solid and the dissolved, but un-ionized, molecules and an equation for the equilibrium between the un-ionized molecules and the ions. For a salt AB, these equations are:

$$(1) \quad \frac{[AB(diss)]}{[AB(solid)]} = K_1;$$

$$\frac{[A^+] \times [B^-]}{[AB(diss)]} = K_2. \quad (2)$$

A very important relationship may be developed from these two equations in the following manner:

In the equation $\frac{[AB(diss)]}{[AB(solid)]} = K_1$, it was assumed that [AB(solid)] had a constant value. As was previously stated, this is not strictly true, but it is sufficiently so for our purpose. From this we can immediately deduce that [AB] is also constant, for

$$[AB(diss)] = K_1 \times [AB(solid)], \text{ from } \mathbf{1};$$

but $[AB(solid)] = \text{constant, call it } K_s;$

therefore $[AB(diss)] = K_1 \times K_s = \text{constant, say } K_m.$

Now let us look at equation **2**:

$$\frac{[A^+] \times [B^-]}{[AB(diss)]} = K_2.$$

But $[AB(diss)] = \text{constant} = K_m$. Therefore we may write $[A^+] \times [B^-] = K_2 \times K_m = \text{constant, say } K_{sp}$.

The new constant is called K_{sp}. It will represent a value we shall call the **solubility product constant.**

To put the above equation in words: **In a saturated solution, at a fixed temperature, the product of the molar concentrations of the ions is a constant, called the solubility product constant.**

It is very important to remember that this applies only to saturated solutions, and *cannot* therefore be applied to any case of equilibrium. For reasons which appear below, this principle applies only to difficultly soluble substances. In spite of its limitations, this relationship is a very important one and will be of great assistance in explaining many of the phenomena which occur in our work.

Limitations of the Solubility Product Principle. — The derivation of the Solubility Product Principle assumes as proven the constancy of the dissolved but un-ionized portion of the molecules. This is not true when other salts are present. Thus in work done by A. A. Noyes, Arrhenius pointed out that the total solubility of thallous chloride ($0.0017N$) in the presence of $0.8N$ potassium chloride is less than the concentration of the un-ionized thallous chloride ($0.00179N$), when potassium chloride is absent.

Coupled with what has been observed concerning the accuracy of the whole mass-action equation from which the solubility product is derived, it would seem that the principle rests on a rather shaky foundation. It is true that for solutions of even moderately soluble strong electrolytes, the solubility product constant is not constant at all. On the other hand, where we deal with a rather insoluble substance, the concentrations of ions, even though the substance be highly dissociated, is comparatively low. The attraction, volume, and hydration effects are not appreciable and the principle holds in semi-quantitative fashion. As previously mentioned, so long as we have a principle which explains a large number of facts in a qualitative fashion, it is valuable for our purposes.*

Precipitation. — Since in a saturated solution the product of the concentrations of the ions is a constant, increasing the concentration of one or both of the ions would give a value greater than the solubility product constant. In other words, the concentrations of the ions are now greater than the values required to saturate the solution. Since we are beyond the saturation point, one of two things must happen; either the solution becomes supersaturated, which seldom happens in qualitative work, or a precipitate forms

* *S-K*, pp. 811–814.

until the solution again becomes saturated and the value of the solubility product is once more attained.

On the other hand, if the product of the concentrations of the ions is less than the value for the solubility product, the solution must be undersaturated. Increase in the concentration of one or both of the ions may now take place until the solubility product value is reached. The solution is again saturated at this point and any further increase in the ion concentrations will cause precipitation as before.

We see then that the solubility product is a criterion of the saturation of a solution. Saturation is the stable condition of equilibrium which both undersaturation and supersaturation approach. It will be helpful to summarize these ideas as follows:

1. **If the product of the concentrations of the ions is less than the solubility product, more of the substance will dissolve, or one or both of its ion concentrations may be increased until the solution is saturated or until the solubility product value is reached.**
2. **If the product of the concentrations of the ions is greater than the solubility product, precipitation occurs until this value is reached.**

Calculating Solubility Products for Simple Salts. — Let us consider an actual case of a salt to get some idea of the numerical values involved. Silver acetate has a solubility of 10.07 g. per liter at 16°. Its molar concentration in a saturated solution, since its molecular weight is 167, is $\frac{10.07}{167}$ or 0.0603 gram mols. Measurements show that it is 70.8 per cent ionized. The concentration of the silver ion is therefore $0.708 \times 0.0603 = 0.0427$. Since for each Ag^+, there is an $C_2H_3O_2^-$ ion, the concentration of the latter ion is also 0.0427. The ionization of the salt is represented as follows:

$$AgC_2H_3O_2 \rightleftarrows Ag^+ + C_2H_3O_2^-.$$

The solubility product equation would therefore be

$$[Ag^+] \times [C_2H_3O_2^-] = K_{sp16°}.$$

Substituting the numerical values just obtained, we have:

$$0.0427 \times 0.0427 = K_{sp16} = 0.00182.$$

This value (0.00182) represents the product of the molecular concentration of the ions at 16°, *when the solution is saturated.* If the solution is undersaturated, the product of the concentrations of the ions is less than 0.00182, and the concentration of one or both of the ions may be increased until this value is reached. At this point, the solution is saturated, and any further increase in the concentration of either or both of the ions will be in excess of the value 0.00182, and precipitation of silver acetate will result. That these facts are so can easily be shown experimentally.

The student should not think all these values are actually determined. Many of them represent values smaller than the most sensitive analytical methods could detect. They are most frequently calculated from other data and are therefore the less accurate.

Calculating the Solubility Products of More Complex Salts. — We saw that in the calculation of the solubility product of $AgC_2H_3O_2$, the operations were quite straightforward. The same is true for all salts made up of two monovalent ions. It is merely a question of dividing the solubility at a given temperature by the molecular weight to get the number of mols per liter and then multiplying this by the degree of ionization to get the number of mols in the ionic form. Since the S.P. value is equal to the product of the concentrations of the ions, multiplying the last obtained value by itself gives us the desired constant.

In the cases of more complex salts, however, we must be more careful not to fall into a trap, for while the calculation involved is simple enough, the necessity for making it is

not always entirely clear to beginners. An example will illustrate the case in point. Let us take silver phosphate, Ag_3PO_4, which ionizes according to the scheme:

$$Ag_3PO_4 \rightleftarrows 3\ Ag^+ + PO_4^{\equiv}.$$

A saturated solution of this salt at room temperature contains 0.0065 g. per liter. Its molecular weight is 418.7. The molar solubility is, therefore, $\frac{0.0065}{418.7} = .0_416$. Since this is an extremely dilute solution, we may consider it to be completely ionized. As a matter of fact, we make the same assumption in calculating practically all solubility product constants, since the principle really holds quantitatively only for very dilute solutions.

From the ionization equation above we see, then, that for every unit or mole of $PO_4^{\equiv}$ ion, there are three units or moles of Ag^+ ion. The concentration $[Ag^+]$ is therefore three times as great as that of the $PO_4^=$ $[PO_4^{\equiv}]$, or is $3 \times 0.0_416 = 0.0_448$. Now, however, we must remember from what has gone before that the Ag^+ ion is effective as the cube of the molar concentration, for our mass-action equation for Ag_3PO_4 is:

$$[Ag^+]^3 \times [PO_4^{\equiv}] = K_{sp} \text{ at this temperature.}$$

Therefore our numerical equation must be:

$$(3 \times 0.0_416)^3 \times (0.0_416) = 0.0_{17}18 = K_{sp} \text{ for } Ag_3PO_4.$$

Another rather interesting fact is to be observed from the above values. Silver iodide is a very much more insoluble salt than silver phosphate. The solubility of the former at room temperature is 0.0_53 g. per liter, which means that it is about 2,200 times more insoluble than the phosphate. When we calculate the solubility product constant for the iodide, however, we find that it is $0.0_{15}17$. In other words, the solubility product constant is 100 times larger for a salt which is 2,200 times more insoluble. This, of course, is a result of the effect of cubing the concentration of the Ag^+ ion in Ag_3PO_4, and among other things, which will be men-

tioned later, it is an outstanding reason why the molar solubilities of different salts cannot be directly predicted from their solubility products.

Common-Ion Effect. — If we increase the concentration of one of the ions to a value that is in excess of the K_{sp}, a very interesting development is to be noted, namely, that the solubility of the salt itself, in this case silver acetate, is actually decreased. Assume that we have a saturated solution of silver acetate and add to it some sodium acetate of strength sufficient to increase the concentration of the acetate ion. The sodium ion does not enter into the consideration. Since now the value of $[Ag^+] \times [C_2H_3O_2^-]$ is greater than the K_{sp}, a precipitate of silver acetate begins to form until the value of the constant is restored. This means that there are less silver ions in the solution. Since each molecule of silver acetate must contain a silver ion, and there are now less silver ions than when the solution was originally saturated, the solubility of silver acetate has been decreased. This was accomplished by adding an ion common to one of the original two. A great deal of use is made of this phenomenon in analytical work, since the total solubility of a salt may be very considerably reduced by this method. It should be remembered, though, that the solubility product value remains the same even if the total solubility becomes smaller.

Without entering into the calculations, the following table shows the changes in the concentrations which take place on addition of sodium acetate to saturated solutions of silver acetate. Column 1 gives the concentration of sodium acetate added to the saturated solution of silver acetate, column 2 the total concentration of the silver acetate in the saturated solution (after the precipitation of some silver acetate has taken place). Columns 3 and 4 show the concentrations of the silver and acetate ions respectively, in the saturated

solution after the addition of sodium acetate, and column 5 shows the value of the solubility product calculated from the others.

TABLE VIII *

$NaC_2H_3O_2$	$AgC_2H_3O_2$	$[C_2H_3O_2^-]$	$[Ag^+]$	K_{sp}
0.00	0.0603	0.0427	0.0427	0.00182
0.061	0.0392	0.0735	0.0258	0.00185
0.119	0.0280	0.1065	0.0167	0.00179
0.239	0.0208	0.1727	0.0109	0.00188

It will be noted in the above table that as the concentration of acetate ion is increased by addition of sodium acetate, the value of the silver ion concentration falls, and with it, of course, the solubility of the silver acetate. The value of the latter drops from 0.0603 mols (with no sodium acetate) to 0.0208 mols, or about one-third the original value.** The constant K_{sp}, it is seen, remains at approximately the same value. Results of the same nature may be obtained by addition of silver nitrate to saturated solutions of silver acetate, simply changing the common ion. In general, it may be said that a difficultly soluble salt may be made less soluble by the addition of a salt which has an ion in common, *provided the concentration of this common ion is increased by the addition.*

Exponential Numbers. — Whereas, up to the present, we have been expressing decimal numbers in their ordinary form, such as 0.00006, or by an abbreviated method, 0.0_46, neither of these methods is the most convenient, either from the

* This table is part of one given by Stieglitz, *J.A.C.S.*, XXX (1908).

** It should not be thought that the reduction of silver acetate to one-third its original value is anything like what may actually be accomplished. It can easily be shown, for example, that the solubility of an "insoluble" sulphide may be reduced as much as 50,000 times by addition of ammonium sulphide.

standpoint of interpretation or from that of arithmetical calculation. Of course, these remarks apply only to very small decimal numbers or very large whole numbers.

When a mathematician wishes to express either a large whole number or a small decimal number, he does it in terms of powers of ten. This necessitates his making his expression a product of two numbers, the first a so-called *digit term* and the second an *exponential term*, which is always the number 10 to some power, depending on the number to be expressed, thus:

$$\begin{aligned} 10 &= 1.0 \times 10^1 \\ 100 &= 1.0 \times 10^2 \\ 1{,}000 &= 1.0 \times 10^3 \\ 32 &= 3.2 \times 10^1 \\ 320 &= 3.2 \times 10^2 \\ 4{,}500 &= 4.5 \times 10^3 \\ 62{,}500 &= 6.25 \times 10^4 \\ 8{,}329 &= 8.329 \times 10^3 \end{aligned}$$

Though it is not absolutely essential, it will be noted that the digit number is always expressed as some whole number less than 10, plus whatever decimal the number requires. The accuracy of most analytical data is generally of such an order that not more than two places of decimals are necessary after the decimal point in the digit term, and in what follows it will be noted that this practice is generally adhered to. If the third term of the decimal is greater than 5, the second term is increased by 1 and the third dropped. If the third term is smaller than 5, it is merely dropped.

The student should particularly note in the above numbers that **the exponent of 10 is equal to the number of places which the decimal point has been moved to the left in the digit number.** Thus, in the number 62,500, the decimal point has been moved four places to the left to give 6.25. The exponent of 10 is therefore 4. This is the simplest way to convert an ordinary number to an exponential one.

A very natural question arises in the student's mind: How am I to express a number between 1 and 10? The answer is that it may be expressed as the number itself times 10 to the zero power, since those who have had algebra will remember that 10 to the zero power (10^0) equals 1. The ordinary convention is to omit the writing of 10^0, leaving it as understood.

Thus far we have confined our attention to numbers greater than one, but we find that in analytical chemistry most solubilities and solubility products with which we are concerned are small fractional numbers, frequently extremely small. How are we to express these? Consider the number 0.005. This may be expressed otherwise as $\frac{5}{1000}$ or $\frac{5}{10^3}$. Mathematicians have proven that for any number a to any power n, $\frac{1}{a^n}$ is the same as a^{-n} (for this proof the student is referred to some standard college text on algebra). This is called one of the *Laws of Exponents*. The expression $\frac{5}{10^3}$, therefore, may be written as 5×10^{-3}. The following examples will illustrate this method of expressing fractional numbers:

$$\begin{aligned} 0.506 &= 5.06 \times 10^{-1} \\ 0.0506 &= 5.06 \times 10^{-2} \\ 0.00506 &= 5.06 \times 10^{-3} \\ 0.000000506 &= 5.06 \times 10^{-7}. \end{aligned}$$

It is to be observed here that **the negative power of 10 is equal to the number of places which the decimal point has been moved to the *right* in forming the digit number.** Thus, in the number 0.00506, to get the digit number 5.06, the decimal point is moved three places to the right. Therefore -3 is the exponent of 10 and the number is written 5.06×10^{-3}.

Mathematicians have taught us several other things about exponential numbers which add a great deal to our conven-

ience in making calculation with them. We shall concern ourselves with only two of these facts. They are:

1. That the product of two exponential numbers may be obtained by adding their exponents **algebraically,** thus, $10^3 \times 10^9 = 10^{3+9} = 10^{17}$, $10^7 \times 10^{-2} = 10^{7+(-2)} = 10^5$, $10^{-3} \times 10^{-7} = 10^{-3+(-7)} = 10^{-10}$.
2. That the quotient of two exponential numbers may be obtained by subtracting their exponents (this is, of course, implied in the above statement, for $10^3/10^2$ is the same as writing $10^3 \times 10^{-2}$).

The student must keep in mind the fact that these rules for exponents apply only to powers of 10 and do not involve the digit number in any way. The digit numbers are treated according to the rules of ordinary arithmetic.

Let us try a few examples to make sure we have the ideas well in mind.

1. Multiply 1.7×10^6 by 3.0×10^4.

   It is best to set the problem down in this fashion:

$$\begin{array}{r} 1.7 \times 10^6 \\ \underline{3.0 \times 10^4} \end{array}$$

   and then set the product of the digit terms beneath the digit terms, and under the exponential terms, their product. For the digit terms $1.7 \times 3.0 = 5.1$, and for the exponential terms $10^6 \times 10^4 = 10^{10}$. Thus we have

$$\begin{array}{r} 1.7 \times 10^6 \\ 3.0 \times 10^4 \\ \hline 5.1 \times 10^{10}. \end{array}$$

2. Divide 6.0×10^7 by 1.5×10^5.

   Set this down by the ordinary method as a quotient:

$$\frac{6.0 \times 10^7}{1.5 \times 10^5}$$

   Then, $\frac{6.0}{1.5} = 4$, and $10^7 \times 10^{-5} = 10^2$, so that our answer is 4×10^2.

Magnitude of Solubility Product. — It is obvious that different salts will have different solubility products. The more soluble the salt, the greater will be the concentrations of its ions and therefore the greater will be the value of their product. In general we may say that the more soluble the salt, the higher will be its solubility product constant. The variation is not mathematically proportionate, however, because the degrees of ionization vary for different compounds. In other words, if one compound were twice as soluble as another and they were both ionized to the same degree and gave the same number of ions per molecule, then the solubility product of one would be just half that of the other. If they are differently ionized, this relation fails. Furthermore, it is obvious that the variation in the values of the solubility product constants will be extremely wide, since the solubility differences in different compounds are so great. The student must keep in mind that these statements apply only to salts of the same valence type. It was shown for Ag_3PO_4 and AgI that the latter has the higher S.P., though much more insoluble than Ag_3PO_4.

The following brief table will give some idea of the numerical values of the solubility products of various common compounds and of the extent of their variation.

TABLE IX *

Compound	K_{sp}	*Compound*	K_{sp}
HgS.....	4.0×10^{-53}	$BaCrO_4$.....	1.6×10^{-10}
CuS.....	8.5×10^{-45}	$BaSO_4$.....	9.0×10^{-10}
PbS.....	4.2×10^{-28}	AgCl.....	1.2×10^{-10}
CoS.....	3.0×10^{-26}	CaC_2O_4.....	1.7×10^{-9}
ZnS.....	1.2×10^{-23}	$CaCO_3$.....	2.8×10^{-9}
MnS.....	1.4×10^{-15}	$BaCO_3$.....	1.9×10^{-9}
$MgNH_4PO_4$..	2.5×10^{-13}	$PbSO_4$.....	1.0×10^{-8}

* These values were taken partially from Treadwell and Hall's *Analytical Chemistry* (1916), pp. 21–22, and from other sources.

Practical Use of the Solubility Product Principle. — Whereas for ordinary purposes of explanation and discussion of reactions in qualitative analysis it is not necessary to go into the actual numerical values for the solubility products, concentrations, and the like, the use of these values is often very important in planning a workable procedure for a system of analysis and points out to the student at the same time the necessity for adhering to the amounts of reagents recommended in his laboratory manual. One or two examples will make this clear.

In the precipitation of the group which contains Cu, Pb, Bi, Cd, Hg, As, Sb, and Sn, most procedures recommend that the concentration of acid for H_2S precipitation be equivalent to 2.5 c.c. of concentrated HCl (12*N*). Since 12*N* HCl contains 12 moles per liter, 2.5 c.c. would contain $12 \times \frac{2.5}{1000} = 0.03$ moles. We have, then, 0.03 moles in 100 c.c., or 0.3 moles per liter. HCl at this concentration is about 90 per cent ionized. The concentration of the H^+ ion $[H^+]$ would be $0.90 \times 0.3 = 0.27$ m/l (moles per liter). Let us see what effect this $[H^+]$ would have upon the precipitation of PbS, the most soluble sulphide (excepting CdS) of the so-called Cu group, and upon ZnS, the most insoluble sulphide of the Fe, Cr, Al, Co, Mn, Ni, Zn group, which for brevity will hereinafter be referred to as the Fe group.

PbS. — When H_2S is passed into a solution containing lead as one of its salts, with HCl of the above strength, until it is saturated at room temperature, the following values must be satisfied:

$$[H^+]^2 \times [S^=] = 1.1 \times 10^{-23}.$$

This is the ion-product constant for H_2S which has been demonstrated by experiment. As calculated above, the $[H^+]$ for this solution is .27, since we may neglect the very minute $[H^+]$ from the dissociation of H_2S itself. We have then:

$$[H^+]^2 \times [S^=] = (0.27)^2 \times [S^=] = 1.1 \times 10^{-23}$$

$$[S^{=}] = \frac{1.1 \times 10^{-23}}{(0.0729)} = 15.1 \times 10^{-23} = 1.51 \times 10^{-22}\ \text{m/l.}$$

From our table, the value for K_{sp} of PbS is 4.2×10^{-28} at room temperature. Knowing that $[S^{=}] = 1.51 \times 10^{-22}$, we can now calculate the $[Pb^{++}]$ which can exist in a solution of the above acid strength when saturated with H_2S:

$$[Pb^{++}] \times [S^{=}] = 4.2 \times 10^{-28}, \text{ but } [S^{=}] = 1.51 \times 10^{-22}$$

$$[Pb^{++}] = \frac{4.2 \times 10^{-28}}{1.51 \times 10^{-22}} = 2.78 \times 10^{-6}\ \text{m/l.}$$

The volume of the solution is 100 c.c., and since we have 2.78×10^{-6} moles in a liter, we will have 0.278×10^{-6}, or 2.78×10^{-7} moles of Pb left in 100 c.c. solution. Let us see how much lead chloride this represents in order to get an idea of the completeness of the precipitation. Each mole of lead weighs 207.2 g., therefore $207.2 \times 2.78 \times 10^{-7} =$ grams of Pb. Since, however, we wish to calculate for $PbCl_2$, we must multiply the weight of Pb by $\frac{PbCl_2}{Pb} = \frac{278.12}{207.2}$. We have then:

$$207.2 \times 2.78 \times 10^{-7} \times \frac{278.12}{207.2} = 2.78 \times 10^{-7} \times 278.12 = 773 \times 10^{-7} = 7.73 \times 10^{-5}.$$

This means that there are 0.0000773 g. of $PbCl_2$ left in the solution, an amount which need not worry us at all.

A frequent error which students make in the precipitation of the copper group with H_2S is to dilute it insufficiently for complete precipitation. It is true that HgS, Bi_2S_3, and CuS, having solubility products of 4.0×10^{-53}, 3.2×10^{-91}, and 8.5×10^{-45} respectively, will be precipitated completely even if the solution is not diluted to 100 c.c. In the case of PbS, however, it can be shown by calculations similar to those above that if the solution containing 2.5 c.c. of HCl is diluted only to 50 c.c., enough lead would remain in solution to give a precipitate in the Fe group and thus give

misleading indications of the presence of Co and Ni, since their sulphides, along with that of lead, are black.

ZnS. — Whereas we must be careful to dilute the solution sufficiently to precipitate all the Cu-group metals, we must on the other hand not dilute it too far, for we may precipitate some ZnS if we do. If the concentration of Zn^{++} and $S^{=}$ are such that $[Zn^{++}] \times [S^{=}] = 1.2 \times 10^{-23} = K_{sp}$ of ZnS, it will be precipitated. Let us see how much Zn^{++} ion this would require. From the previous calculation, with 2.5 c.c. HCl in 100 c.c. $[S^{=}]$ was 1.51×10^{-22}. We may then write:

$$[Zn^{++}] \times (1.51 \times 10^{-22}) = 1.2 \times 10^{-23}$$

$$[Zn^{++}] = \frac{1.2 \times 10^{-23}}{1.51 \times 10^{-22}} = 0.795 \times 10^{-1} = 0.0795 \text{ m/l.}$$

Since the usual strength of solutions given for analysis contains about 0.0045 m/l of Zn^{++} ion, no zinc would be precipitated at 100 c.c. If the $[Zn^{++}]$ is raised to 0.024 m/l and the solution diluted to 200 c.c., ZnS will begin to precipitate. This can easily be seen from the following considerations: Dilution to 200 c.c. reduces $[H^{+}]$ to $\frac{1}{2}$ its former value. $[H^{+}]^2$ then becomes $\frac{1}{4}$ and $[S^{=}]$ is 4 times as large in consequence. This means that $[Zn^{++}]$ is $\frac{1}{4} \times 0.0795$ m/l = 0.0199 m/l. Since the original concentration of Zn^{++} was 0.024 m/l, some ZnS would precipitate. From the above considerations, it is clear that the proper acid concentration at the beginning of the copper-group procedure is quite important.

Precipitation of $Mg(OH)_2$. — Another frequently cited illustration of the practical use of the Solubility Product Principle is the prevention of the precipitation of $Mg(OH)_2$ along with the Fe-group sulphides and hydroxides, by addition of NH_4Cl. If the Mg^{++} ion is precipitated at this point, it will, of course, be filtered and not only mislead us in our

conclusions about the Fe group, but make it difficult or impossible to find Mg^{++} in its proper place.

The K_{sp} for $Mg(OH)_2$ is 1.2×10^{-11}. Until $[Mg^{++}] \times [OH^-]^2 > 1.2 \times 10^{-11}$, no Mg^{++} will be precipitated. The solutions given to students for analysis are generally made from $Mg(NO_3)_2$ with about 1.5 g. of Mg per liter. This means that with respect to Mg, the solution contains $\frac{1.5}{24}$ m/l = 0.0625 m/l. The $Mg(NO_3)_2$ at this concentration is about 70 per cent ionized. The $[Mg^{++}]$ is therefore $0.0625 \times 0.70 = 0.04375 = 0.044$ m/l. From above, $[Mg^{++}] \times [OH^-]^2 = 1.2 \times 10^{-11}$, we can now find the $[OH^-]$ necessary to start the precipitation of $Mg(OH)_2$:

$$([Mg^{++}] = 0.044) \times [OH^-]^2 = 1.2 \times 10^{-11}$$

$$[OH^-] = \sqrt{\frac{1.2 \times 10^{-11}}{0.044}} = \sqrt{27.8 \times 10^{-11}}$$

$$= \sqrt{2.78 \times 10^{-10}}$$

$$= 1.67 \times 10^{-5}.$$

Now let us see what $[OH^-]$ is present when NH_4OH with no ammonium salt is added at the beginning of the Fe group. Assume that a 2-c.c. excess of $2N$ NH_4OH is added and that the total volume of the solution is 20 c.c. The NH_4OH is $\frac{2}{20} \times 2 = 0.2N$ or molar. NH_4OH at this concentration is about 1.0 per cent ionized. Therefore, $[OH^-] = 0.2 \times 0.01 = 0.002 = 2 \times 10^{-3}$ m/l. Since, as calculated above, it requires only 1.67×10^{-5} m/l to start precipitation of $Mg(OH)_2$, the normal addition of NH_4OH at the beginning of the Fe group would precipitate some $Mg(OH)_2$. This is prevented by the addition of NH_4Cl.

Let us examine the effect of adding 5 c.c. of $6N$ NH_4Cl in a total volume of 20 c.c. The concentration of NH_4Cl is $\frac{5}{20} \times 6 = 1.5N$ or m/l. At this concentration, NH_4Cl is about 75 per cent ionized. Therefore, $[NH_4^+] = 1.5 \times 0.75 = 1.125$ m/l. The $[NH_4^+]$ from the NH_4OH would be the same

as the $[OH^-]$ which was calculated to be 2×10^{-3} m/l. The total $[OH^-]$ is then $1.125 + 0.002 = 1.127$.

Now calculate the ionization constant (x) for NH_4OH in order to find the effect of the increased NH_4^+ ion of the NH_4Cl. We know that:

$$\frac{[NH_4^+] \times [OH^-]}{[NH_4OH]} = K_{NH_4OH}.$$

From above, $[OH^-]$ and therefore $[NH_4^+]$ of the $NH_4OH = 0.002$. Since we originally had 0.2 molar NH_4OH in a 20-c.c. volume, the $[NH_4OH] = 0.2 - 0.002 = 0.198 = 1.98 \times 10^{-1}$ Therefore:

$$\frac{([NH_4^+] = 2 \times 10^{-3}) \times ([OH^-] = 2 \times 10^{-3})}{([NH_4OH] = 1.98 \times 10^{-1})} = \frac{4 \times 10^{-6}}{1.98 \times 10^{-1}} =$$

$$\frac{4 \times 10^{-5}}{1.98} = 2.02 \times 10^{-5} = 0.00002 = K_{NH_4OH}.$$

When NH_4Cl is added, $[NH_4^+]$ is increased; and since K must remain constant, $[OH^-]$ is diminished. The only way in which $[OH^-]$ can diminish is by formation of molecular NH_4OH, which means that $[NH_4OH]$ is increased. Relatively it increases but little. Its maximum, if the NH_4OH were not dissociated at all, would be 0.2, since this was the total original concentration of the ammonium hydroxide. Let us assume that, by virtue of the addition of the NH_4Cl, $[NH_4OH]$ is raised to 0.199. Remembering that the total $[NH_4^+]$ was calculated to be 1.127, we may write:

$$\frac{([NH_4^+] = 1.127) \times [OH^-]}{([NH_4OH] = 0.199)} = K_{NH_4OH} = 0.00002.$$

We may calculate from this the value to which $[OH^-]$ has been depressed by the addition of NH_4Cl:

$$[OH^-] = \frac{0.0_42 \times 0.198}{1.127} = \frac{2 \times 10^{-5} \times 1.98 \times 10^{-1}}{1.127} =$$

$$\frac{3.96 \times 10^{-6}}{1.127} = 1.62 \times 10^{-6} = 0.0_5162.$$

Since the $[OH^-]$, without NH_4Cl, was 2×10^{-3} and after the addition is 1.62×10^{-6}, the $[OH^-] = \frac{1.62 \times 10^{-6}}{2 \times 10^{-3}} = 0.81 \times 10^{-3} = 0.00081$ or about $\frac{1}{1235}$ of what it originally was. This is by far too little to precipitate $Mg(OH)_2$.

The use of NH_4Cl to reduce the concentration of the OH^- ion is another well-known example of the common-ion effect.

SUMMARY

We have just learned that:

1. In a saturated solution, at a fixed temperature, the product of the concentrations of the ions is a constant.
2. This applies strictly mathematically only to dilute solutions of weak electrolytes, but is nevertheless very valuable in a qualitative way.
3. If we know the concentrations of the ions in a solution and the value of the solubility product for a given salt, we can predict whether it will give a precipitate or not.
4. The values for the solubility products of simple and complex salts may be calculated from their solubilities.
5. The concentration of a given ion in a solution may be depressed by the addition of a compound with a common ion in higher concentrations than that present.
6. This is called the **common-ion effect.**

QUESTIONS

1. Is the concentration of the solid phase in equilibrium with its saturated solution a constant? Interpret your answer.
2. State the Solubility Product Principle.
3. Why does the Solubility Product Principle hold only at a fixed temperature?
4. Derive a mathematical expression for the solubility product.
5. What are the limitations of the Solubility Product Principle? Does this affect its usefulness in a qualitative way?
6. Explain how the solubility product is used as a criterion of precipitation.

7. Given the following solubilities in grams per liter at room temperature, calculate the solubility products.

Substance	*Solubility*	*Sol. product* *
		Ans. —
$AgCl$	1.5×10^{-3}	1.2×10^{-10}
Ag_2SO_4	8.0	7.0×10^{-5}
$BaCrO_4$	3.8×10^{-3}	2.3×10^{-10}
CaC_2O_4	8.0×10^{-3}	3.8×10^{-9}
CaF_2	1.6×10^{-2}	3.4×10^{-11}
Hg_2Cl_2	3.8×10^{-4}	2.0×10^{-18}
$MgNH_4PO_4$	8.6×10^{-3}	2.5×10^{-13}
$Pb_3(PO_4)_2$	1.4×10^{-4}	1.5×10^{-32}
$SrSO_4$	1.1×10^{-1}	3.6×10^{-7}
ZnS	3.3×10^{-10}	1.2×10^{-23}

8. Assuming that a solution at the beginning of the analysis for the Fe group of metals has 0.05 m/l of $(NH_4)_2S$ which is 53 per cent dissociated, calculate the amount of $ZnCl_2$ left after the ZnS is filtered and the solution evaporated to dryness. The K_{sp} of ZnS is 1.2×10^{-23}.

Ans. 6.2×10^{-21} g. $ZnCl_2$.

9. The solubility of $BaCrO_4$ at 20° C. is 0.0037 g. per liter. If, in a total volume of 100 c.c., there is present 0.5 c.c. of $0.2N$ K_2CrO_4, which is 80 per cent ionized, what will be the concentration of barium left in solution after precipitation? Assume that the $BaCrO_4$ is completely ionized.

Ans. 5.4×10^{-7} m/l.

10. What is meant by the *common-ion effect?* Give two illustrations taken from your procedure and discuss their application.

* The student should not be confused by the fact that these values do not agree in some cases with those on p. 107. They are taken at different temperatures.

CHAPTER VI

EQUILIBRIUM AND IONIC CONCENTRATIONS

The Big Two. — Up to this time, we have been preparing and gathering the tools which we will use in making our explanations of analytical phenomena. We have seen the reasons for the belief in the ionization theory. We have learned the principles and some applications of equilibrium, particularly ionic equilibrium. We have studied the principle of the solubility product and its application. We thus have the means at hand to offer a reasonable explanation for any of the phenomena of precipitation and solution which occur in ordinary analytical work, with a few exceptions which will be considered separately.

It was noted that all ionic equilibria are reversible, but our interest does not lie so much in the reversibility of a reaction as it does in the means of causing the equilibrium to go to completion in one direction or the other. We have noted that pressure, temperature, and concentration in general are the factors used to shift equilibria toward completion. Only the last is consistently applied in analytical work. The ways in which changes in concentration affect ionic equilibria will be considered in detail after some thought has been given to the things to be looked for in general, when offering a theoretical explanation.

One of the outstanding and most frequently used methods of producing a change in concentration of ions is the formation of a weak electrolyte. As previously stated, a weak electrolyte is one whose molecules show only a small tendency toward dissociation. Take the case of acetic acid, for example. In a normal solution of the latter, of the whole

amount present, only 1 per cent approximately is in the ionic form. The acetic acid molecules do *not* tend to dissociate, and the H^+ and $C_2H_3O_2^-$ ions *do* tend to combine.

It is obvious that acetic acid itself need not be added to a solution in order that it be present. If we mix compounds that offer greater concentrations of the H^+ and $C_2H_3O_2^-$ ions than correspond to the ionization concentrations of acetic acid, the latter will be formed by association of the excess ions. Thus, if hydrochloric acid and sodium acetate, both well dissociated, are put into the same vessel, the concentrations of the H^+ and $C_2H_3O_2^-$ ions are much greater than would satisfy the equation

$$\frac{[H^+] \times [C_2H_3O_2^-]}{[HC_2H_3O_2]} = \text{K at room temperature.}$$

The result is that something must happen to reduce the concentrations to such values as will satisfy the constant for acetic acid. What happens is combination of the H^+ and $C_2H_3O_2^-$ ions, which decreases $[H^+]$ and $[C_2H_3O_2^-]$ and increases $[HC_2H_3O_2]$. This is all in the direction of satisfying the constant. The net result is that a considerable quantity of molecular acetic acid has been formed and the concentrations of the hydrogen and acetate ions have been considerably reduced.

These circumstances are clearly not confined to acetic acid, but apply to every case of a weakly ionized substance. We may summarize, then: **If the ions of a weakly ionized substance are present in a solution in greater concentrations than correspond to the ionization of the substance, molecules of it will be formed from the ions and the ion concentrations consequently reduced.** A corollary to this fact becomes apparent: If there are two weak electrolytes present, the less weakly ionized will be formed at the expense of the other.

The formation of a weakly ionized substance offers a ready means of causing an equilibrium to go to completion in a

given direction, and will be one of the first things we shall seek in making an explanation. **In a great majority of the cases, the nub of the explanation lies in the formation of a weakly ionized compound.** We were taught, when children, that we must seek the weak link to find where the chain gave way. So now, in trying to make subsequent explanations of various phenomena which occur in analytical chemistry, we shall always **look for the weak compound.** The importance of this idea will be evident in the explanations made later in this work.

The other of the two big things to look out for is the solubility product principle. Many of the explanations involve the formation or solution of a precipitate, and thus the solubility product idea. In any case that concerns itself with such action, we must first look for a weakly ionized substance. Finding one or not, we should then **apply the solubility product principle,** if a precipitate is involved. There are few explanations which are not amenable to this simple method of procedure. It should, therefore, be the student's first thought, after acquiring a thorough working knowledge of these two principles, to attempt the application of one or both of them in starting an explanation:

1. **Look for the weak compound.**
2. **Apply the solubility product principle.**

Types of Equilibrium Shift. — Having given some thought to what we must be on the lookout for, it will be our purpose now to consider the different specific types of phenomena which bring about the disturbance of an equilibrium.

In general, any of these cases may be looked upon as an application of Le Chatelier's principle. The use of this principle as such in ionic equilibria is not always as obvious as might be desirable, because of the number of factors involved. We can, however, state the principle in a form which is particularly applicable to cases of ionic double decompositions, as follows: **Ionic double decompositions**

shift in the direction toward which there is a decrease in ion concentration.

The various methods by which the concentrations of the ions can be decreased may be summarized as follows:

1. Formation of an insoluble compound.
2. The addition of a common ion.
3. Formation of a slightly ionized compound.
   - *a.* By displacement from its salts by a stronger acid.
   - *b.* By neutralization.
     - (1) Amphoteric compounds.
   - *c.* By hydrolysis.
4. The formation of a complex ion.
5. The discharge or change of charge on an ion (oxidation and reduction).

Each of these cases, of which, as has already been indicated, the first two are by far the most important, will now be considered in detail.

1. Equilibrium Shift by Formation of an Insoluble Substance. — If we combine two electrolytes, AB and CD, which react to form two others, AD and BC, according to the equation

$$AB + CD \rightarrow AD + BC,$$

a condition of equilibrium is instantly established. If all four are soluble substances, there will be definite amounts of each present after the establishment of equilibrium. AB and CD dissociate; the various ions collide, and as a result of some of these collisions, AD and BC are formed. AD and BC dissociate in turn, and the reverse reaction results from the collisions of the ions. This was the case for the reaction between ammonium thiocyanate and ferric chloride, previously considered. If, however, one of the substances is a so-called insoluble one, i.e., if it is sufficiently insoluble to form a precipitate, an entirely different state of affairs obtains. Suppose that, in the general case above, AD is an

insoluble substance and precipitates. All the particles of it which are in precipitate form are molecules and no longer ionic. The reaction in either direction, we remember, is due to ionic collisions. For this purpose the molecules of the precipitate are useless. They may as well be outside the containing vessel. The result is obvious. An enormous number of A ions and D ions have been removed from the field of action. The chances for the collision of A ions with B ions to form AB, and of C ions with D ions to form CD, have been greatly reduced owing to the reduction of A ions and D ions. The reverse reaction, therefore, has been greatly retarded; not so for the forward action (at least, momentarily). The collisions to form AD and BC continue, and more insoluble AD forms. This progresses until (for all practical purposes) the reaction has gone to completion in the direction of the formation of AD.

Actually, the reaction does not go to completion. The reason for this is that while we speak of "insoluble substances," there are none such. No matter how insoluble the compound may be, we believe it to have some solubility. Since there is some dissolved, it will form ions. Incidentally *the ionization may be considered to be* 100 *per cent*, since, owing to the insolubility of the compound, the solution is very dilute. These ions, A and D in the case considered, collide with the others, B and C, and as a result the reverse reaction takes place to some extent. To all intents and purposes, this is negligible. We say, therefore, that the reaction "goes to completion."

Let us look at this type of reaction from another point of view. The solubility product of the compound AD may be represented by the following expression:

$$[A^+] \times [D^-] = K_{sp}.$$

Consider that the dissociation occurs during a finite period of time, though we cannot measure it. AB then furnishes

A ions and B ions, and CD furnishes C ions and D ions. At first the concentrations of the A^+ ions and D^- ions will be less than K_{sp} (at room temperature) for AD. As the concentrations increase, the constant is exceeded, and AD precipitates to reach the value of the constant again. While this happens, more A ions and D ions are being formed, and more AD precipitates. The process continues until the value for K_{sp} is satisfied, and not enough A ions and D ions are being supplied to exceed it. If AD is a nearly insoluble substance, this will occur only when the reaction has essentially gone to completion.

It is of interest to note that this is one class of explanation which does not necessitate the formation of a weakly ionized compound. We do, however, apply the Solubility Product Principle.

2. Equilibrium Shift by the Formation of a Weakly Ionized Compound. — *a. By Displacement from Its Salts by a Stronger Acid.* — The previous case dealt with the formation of a precipitate. The one now to be considered deals with the opposite case of the dissolving of a precipitate. These two are the most commonly occurring phenomena in qualitative analysis.

Consider a solid substance AB in equilibrium with its saturated solution. We have then two equilibria: the one, between the solid and the dissolved molecules; the other, between the dissolved molecules and the ions which they form. This may be represented:

$$\underset{\text{(solid) (1)}}{AB} \rightleftarrows \begin{matrix} \underset{\text{(dissolved) (2)}}{AB} \rightleftarrows \underset{\text{(ionic)}}{A^+ + \boxed{B^-}} \\ HX \rightleftarrows X^- + \boxed{H^+} \end{matrix} \rightleftarrows HB \text{ (mol.)}.$$

Let us call the solid $\rightleftarrows$ molecular equilibrium **1** and the molecular ionic equilibrium **2**.

Suppose that to AB a strongly ionized acid HX is added, as shown above. Let the acid HB be a weakly ionized one. Here we have the **weak compound,** the key to our explanation. Since HB is a weakly ionized compound, the H ions and B ions will not have any great tendency to dissociate once they have met. They remain largely in the molecular form. Since B has left the ionic form in large part, the opportunities for B ions to strike A ions have been greatly reduced, and the formation of AB molecules greatly retarded. On the other hand, the AB molecules need not collide with anything in order to dissociate. They continue to form as rapidly as before. The motion (equilibrium **2**) in the direction (→) is as rapid as before. The opposite motion (←) has been retarded. The result is, obviously, that the amount of molecular AB has been considerably reduced. What does this mean with respect to equilibrium **1**? Since the molecular AB has been reduced, the motion (←) in equilibrium **1** must be retarded. Solid AB has as yet not been affected, and the motion (→) in equilibrium **1** continues as before. Since the motion (→) is therefore more rapid than the motion (←), there is a resulting decrease in the solid AB. In other words, the solid dissolves. If sufficient HX is added, all of the AB solid may thus be dissolved.

The above explanation views the case without the application of the Solubility Product Principle. The latter may be applied as follows. In the saturated solution the relation

$$[A^+] \times [B^-] = K_{sp} \text{ (at a given temperature)}$$

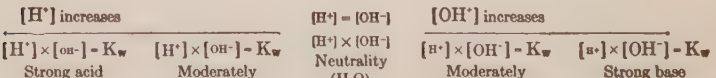
holds. When HX is added and HB (the **weak compound**) forms, $[B^-]$ falls below the value necessary to satisfy the constant K_{sp} (the **S. P. Principle**). This means that the solution becomes momentarily unsaturated. More AB dissociates to saturate the solution again, but the B^- ions are removed as fast as they are formed, keeping the solution undersaturated. Since the solution is continually being made

undersaturated, there will be a shift in both equilibria in the direction (→), until all the solid AB is dissolved, provided enough HX is added.

Equilibrium Shift by the Formation of a Weakly Ionized Compound. — *b. Amphoteric Hydroxides.* — When we speak of acids, we generally do not consider the OH^- ion as associated with them. Similarly for bases, we do not think of the H^+ as being present. Actually the OH^- ion is present in all acids and the H^+ in all bases. The fact that a substance is acid simply means that the H^+ ions so far outnumber the OH^- ions that the solution as a whole exhibits acid properties. The mere fact that water is present, as it must be in any acid or base, is assurance that both H^+ and OH^- ions are present. Though only to a very small extent, water *is* dissociated. The equilibrium equation for water alone is:

$$\frac{[H^+] \times [OH^-]}{[HOH]} = K,$$

where both $[H^+]$ and $[OH^-] = 1 \times 10^{-7}$. Since [HOH] is practically constant, we may say $[H^+] \times [OH^-] = K_w$, the constant $K_w = 1 \times 10^{-14}$. Obviously, when a strong acid is present, $[H^+]$ is very large. To keep the value of K_w at 1×10^{-14}, $[OH^-]$ consequently is negligibly small. The same type of reasoning applies to bases. As the $[H^+]$ decreases (in other words, as the acid grows weaker), the $[OH^-]$ becomes larger and larger, until a point is reached where $[OH^-]$ is equal to $[H^+]$. As we pass beyond this point, $[H^+]$ decreases as $[OH^-]$ increases, and we are on the basic side of neutrality, the basic tendencies becoming increasingly strong. These ideas may be summarized in a diagram, as follows:



It might be said, on first thought, that as we approach the region of the dissociation of water, the concentration of H^+ and OH^- ions is negligible. In many cases this is so, but in many others the small ionization of water plays a very important rôle in the phenomena which occur, as will be seen under hydrolysis.

From what has gone before, it is clear that, as the H^+ ion-forming tendencies decrease, the OH^- ion-forming tendencies increase, and vice versa. It is not surprising, then, to find many compounds which, like water, show both tendencies distinctly. They are the so-called *amphoteric hydroxides*, though the name *hydroxides* is misleading. They are acids as well.

The name generally indicates whether the OH^- tendency predominates. Thus we have *aluminium hydroxide* (rather than *aluminic acid*), in which the basic tendencies predominate. On the other hand, we have *arsenious acid* (rather than *arsenious hydroxide*). The important fact is, however, that amphoteric hydroxides show both tendencies — hence their duplex properties. The very name *amphoteric* comes from the Greek *amphoteros*, which means "both."

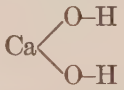
TABLE X

Groups

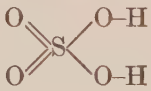
Series	M_2O	MO	M_2O_3	MO_2	M_2O_5	MO_3	M_2O_7
1	Li	**Be**	B	C	N	O	F
2	Na	Mg	**Al**	**Si**	P	S	Cl
3	K	Ca				**Cr**	Mn
4	Cu	**Zn**			**As**		Br
5		Sr					
6	Ag	Cd		**Sn**	**Sb**		**I**
7		Ba					
8							
9		Hg		**Pb**	Bi		

A brief examination of the abbreviated periodic table shown on page 123 will not only help us to understand the occurrence of amphoteric compounds, but will also give us a more definite basis on which to remember those that are amphoteric. Groups 0 and 8 are omitted because they do not particularly enter into our consideration of amphoteric compounds. Only the common elements are included.

Structurally, all oxygen acids and bases are alike. All may be written in the form of hydroxides. It is merely a question of whether the H or the OH group is dissociated. Thus calcium hydroxide is written:



the OH's being dissociated; and sulphuric acid is written:

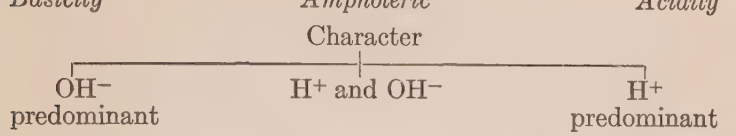


the H's being dissociated.

In considering Table X, let us then confine ourselves to the "OH" type of compound and take series 2 as most representative, for it will be remembered that the first series contains the elements which show exceptional properties.

Consider then the "hydroxides" of sodium, magnesium, aluminium, silicon, phosphorus, sulphur, and chlorine. Sodium and magnesium hydroxides are strong bases. Sulphuric and perchloric acids are strong acids. In other words, on the left we have strong OH^- forming tendencies, and on the right, strong H^+ tendencies. Phosphoric and silicic acids are weak acids, silicic being very slightly amphoteric. Aluminium hydroxide is distinctly amphoteric. The change from acidity to alkalinity is gradual, and approximately in the center we have those compounds which show both basic and acidic tendencies, the amphoteric hy-

droxides. In any series of the periodic table, going from left to right, we have an arrangement similar to a previous diagram:



Let us now consider what happens as we pass down through a group or family of related elements, such as Group V in the periodic system, consisting of nitrogen, phosphorus, arsenic, antimony, and bismuth. The hydroxides of nitrogen and phosphorus are decidedly acid in character; the lower valence of arsenic is amphoteric on the acid side; the lower valence of the hydroxide of antimony is also amphoteric; and the hydroxide of bismuth is basic. Obviously, then, as we pass down a group, the basicity increases as the atomic weight becomes larger, the amphoteric elements again being approximately midway.

We have then two tendencies in the system:

1. Increasing acidity from left to right,
2. Increasing basicity from top to bottom.

The net result of these two tendencies is to throw the amphoteric elements near the center of the table, so that the elements near a diagonal drawn from beryllium in Group II to antimony in Group V are the ones whose acidic and basic tendencies are most marked. The common amphoteric elements are zinc, aluminium, divalent tin and lead, trivalent chromium, arsenic, and antimony. Since many of the elements in this section of the periodic table are not common in occurrence, the full extent of the amphoteric character among the elements is not generally appreciated.

It is to be noted that, in speaking of the amphoteric character of elements showing more than one valence, a definite

valence was specified, generally the lower. When an element is capable of forming more than one hydroxide, the hydroxides vary in basicity. The hydroxides of the higher valences generally are the more acidic, those of the lower valences more basic. Again, where there are more than two valences, the lowest will be basic in character, the highest will be acidic, and the intermediate will tend toward being amphoteric. Chromic acid, representing hexavalent chromium, is strongly acid; divalent chromium hydroxide is exclusively basic; and chromic hydroxide is amphoteric.

The tetrahydroxides of tin and lead are both acidic, whereas their dihydroxides, while both show an acid character, are more basic than acidic. The higher acids of both arsenic and antimony are both decidedly acid, whereas their trivalent hydroxides are both amphoteric.

In general, we may say that a multivalent element in its low valences tends to be like the elements on the left-hand (low-valence) side of the periodic table, and that in its higher valences it resembles the acidic elements on the right-hand (high-valence) side of the table.

Summarizing the criteria for amphoteric character, we have then three facts to ascertain in reaching a conclusion:

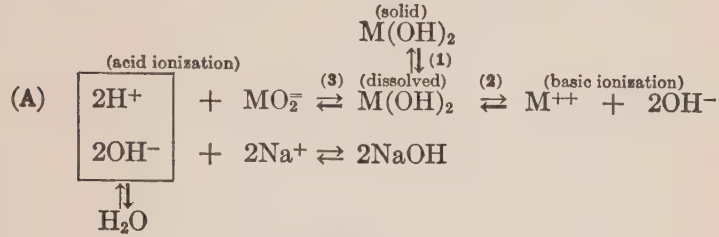
1. Position in series across periodic table
2. Position in group down periodic table
3. Valence of the element (if more than one valence).

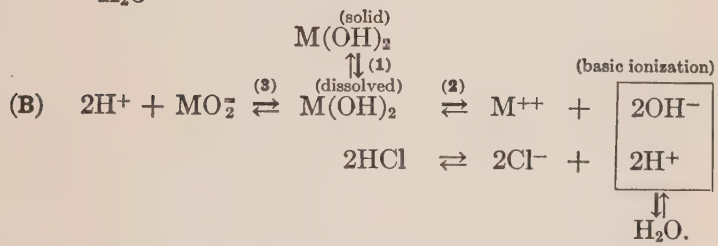
Having seen something of the reasons for expecting the existence of amphoteric hydroxides, let us now consider the ways in which these hydroxides show their amphoteric character.

If a substance can act both like a base and like an acid, it should be capable of neutralization in two ways — either by another acid or by another base. This is the most outstanding property of amphoteric hydroxides.

Let us consider the case of a metal which can form an amphoteric hydroxide $M(OH)_2$. Since this compound acts

also as an acid, it may be written H_2MO_2. All metallic hydroxides are insoluble except the alkalies and the hydroxides of calcium and barium, so for an amphoteric hydroxide which has been precipitated from a solution, the following equilibria are set up:





Case **A** shows the circumstances when a strong base is added. The solid substance $M(OH)_2$ is in equilibrium with the dissolved molecules (Eq. **1**) which are in turn in equilibrium with two sets of ions, constituting the basic ionization (Eq. **2**) and the acid ionization (Eq. **3**). As the strong base is added, the hydrogen ions of the $M(OH)_2$ unite with the hydroxyl ions of the base (which are being supplied in large quantity) to form the **weak compound** water. With the removal of the hydrogen ion from $M(OH)_2$, the solution becomes undersaturated with respect to the $M(OH)_2$ (**the S. P. Principle**). As a result, more $M(OH)_2$ ionizes, in turn causing equilibria **1** and **2** to shift in the directions indicated by the heavier arrows, as explained in similar cases before. Addition of sufficient NaOH will cause complete solution of the hydroxide.

This may be looked at from another point of view. Since $M(OH)_2$ supplies H^+ and OH^- ions, the expression

$$[H^+] \times [OH^-] = K_w$$

must be satisfied, as well as the expression

$$[H^+]^2 \times [MO_2^-] = K_{sp},$$

where $[H^+]$ is the same in both cases.

If a strong base is added, $[OH^-]$ becomes very large. To satisfy K_w, $[H^+]$ must therefore become vanishingly small. This means that

$$[H^+]^2 \times [MO_2^-] < K_{sp},$$

and the solution is undersaturated. To return to the normal state of saturation, $M(OH)_2$ dissolves. The extent of this action depends on the $[OH^-]$ from the base.

The case outlined in **B** is explained in exactly the same fashion, except that here, instead of the H^+ ions of $M(OH)_2$ being involved, the OH^- ions form the weak compound.*

It is important for the student to remember that an amphoteric hydroxide *always* dissociates *both* as an acid and as a base, because it is a common misconception that such a compound ionizes only as a base in the presence of an acid and only as an acid in the presence of a base.

Equilibrium Shift by the Formation of a Weakly Ionized Compound. — *c. Hydrolysis.* — Neutralization of acids by bases was explained by saying that weakly ionized water was formed, causing a shift in the equilibrium toward the formation of the salt and water. So for the case of sodium hydroxide and hydrochloric acid:

$$Na^+ + OH^- + H^+ + Cl^- \rightarrow Na^+ + Cl^- + H_2O.$$

* The question of self-neutralization of amphoteric hydroxides has been dispensed with as unnecessary in elementary work. An excellent treatment of this question is to be found on page 187 of Stieglitz's *Qualitative Analysis* (1919), Vol. I.

It will be noted that all the compounds involved, except water, are highly ionized. Since there are free sodium ions from the ionization of NaCl, and free hydroxyl ions from the small ionization of water, these ions will come into contact and form sodium hydroxide. The latter ionizes highly, and therefore only a very minute quantity of molecular NaOH will be formed. The same is true for the hydrochloric acid. In other words, the action in the reverse direction ($\leftarrow$) is negligible. Since the sodium hydroxide and hydrochloric acid are about equally ionized, the H^+ and OH^- ions supplied by the water will be used up about *equally* to form what traces of hydroxide and hydrochloric acid are present. There would, therefore, be no excess of H^+ or OH^-, and the solution would be neutral.

Hydrolysis of a Salt of a Weak Base and a Strong Acid. — Let us now consider the case in which a weak base is neutralized by a strong acid:

$$M^+OH^- + H^+ + X^- \rightleftarrows M^+ + X^- + H_2O,$$

where MOH is a weak base.

The same explanation might be applied as in the case of the strong acid and strong base — weakly ionized water is formed and there is a shift in the equilibrium toward the formation of water — but this does not complete the story. Whereas, considering the reverse reaction, the H^+ ions of the water will form little un-ionized acid with the X^- ions of the highly ionized salt (since the acid is highly ionized), the same is not true for the base. The M^+ ions from the highly ionized salt meet the OH^- ions from the water, but they do not redissociate to any great extent because the base is weakly ionized and tends to remain in the molecular state. This uses up the OH^- ions of the water, but lets the H^+ ions go free. The OH^- ions are used until the ionization constant for the base is satisfied. The weaker the base, the

more OH^- will be used. To supply these OH^- ions, water has dissociated further, thus increasing the supply of free H^+ ions in the solution. When equilibrium is established, there is a considerable excess of H^+ ions and the solution reacts acid. The reverse action here is *not* negligible. It is called *hydrolysis*. It is a *double decomposition* in which water is one of the reacting substances, and is the reverse of neutralization.

We may say further that the salt of a strong acid and a weak base is *hydrolyzed* by water to give an acid reaction. The fact that the hydrolysis was considered as the reverse of neutralization does not affect the case in any way. The statement of the equation might have been written:

$$HOH + M^+ + X^- \rightleftarrows MOH + H^+ + X^-,$$

but the reasoning would have been the same.

Hydrolysis of a Salt of a Strong Base and a Weak Acid. — For the sake of clarity, let us consider this case from the reverse point of view. Assume that a quantity of a salt MA is dissolved in water. Let the acid HA from this salt be a weak acid and the base MOH a strong base. The reaction may be represented as follows:

$$M^+ + A^- + HOH \rightleftarrows M^+ + OH^- + H^+A^-.$$

The small number of OH^- ions from the water in their migrations meet the M^+ ions of the highly dissociated salt. They tend to form small amounts of molecular MOH, but, this being a strong base, the M^+ and OH^- ions are practically completely returned.

Similarly the great number of A^- ions from the salt meet the few H^+ ions from water and form the acid HA. This is a weak acid, however, and the H^+ and A^- ions are not returned to the solution. This means that more water must

dissociate to replace the H^+ ions used up in the acid, so that the equilibrium

$$HOH \rightleftarrows H^+ + OH^-$$

remains satisfied. Since there were a great many A^- ions from the high dissociation of the salt, H^+ ions will continue to be used until the equilibrium

$$HA \rightleftarrows H^+ + A^-$$

is satisfied. When this is accomplished, there is a large excess of OH^- ions from the water. The result is that the solution reacts alkaline.

We may say, then, that a salt of a strong base and a weak acid is hydrolyzed by water to give an alkaline reaction.

Both of the above cases were considered from a general point of view. Let us now consider a specific case in a slightly different way to help clear up any doubts. It makes no difference whether the case under consideration is a salt of a strong base and a weak acid or vice versa. The reasoning is the same. Consider the neutralization of acetic acid by sodium hydroxide, or the hydrolysis of sodium acetate, which is the same thing. The equation is

$$HC_2H_3O_2 + Na^+ + OH^- \rightleftarrows Na^+ + C_2H_3O_2^- + H_2O.$$

Acetic acid is a weak acid, about 1 per cent ionized in tenth normal solution. Sodium hydroxide is about 85 per cent ionized at the same concentration, and sodium acetate is ionized 80 per cent. Water, of course, is extremely little ionized.

As the reaction toward the right proceeds, the hydroxide ion concentration is greatly decreased from the concentration furnished by NaOH to that furnished by water, which is almost zero. The concentration of the hydrogen ion is also decreased from that of acetic acid to that of water, though this is not so great a decrease, since acetic acid is weak in itself. Considering the reverse reaction, the hydroly-

sis, there is a decrease in the acetate ion from that furnished by highly ionized sodium acetate to that of the weakly ionized acetic acid, though this decrease is very much smaller than the decrease of hydroxide ion toward the right. Since sodium hydroxide is highly ionized, there is practically no tendency toward formation of it.

Summarizing, we have toward the right a large fall in hydroxide ion concentration and a very moderate fall in hydrogen ion concentration. Toward the left we have only a fall, though considerable, in the acetate ion concentration. The net result is that the major tendency is toward the right, but *not completely* so. The reverse reaction does take place to a small extent, and since the acetic acid is weak and the sodium hydroxide strong, there will be more hydroxide than hydrogen ions and the solution will be basic.

Hydrolysis of a Salt of a Weak Base and a Weak Acid. — Finally, let us consider a salt which is formed from a weak base and a weak acid, say ammonium cyanide, NH_4CN:

$$NH_4^+ + CN^- + HOH \rightleftarrows NH_4OH + HCN.$$

The ammonium cyanide is a salt and highly ionized. Ammonium hydroxide is a base of about 1 per cent ionization, while water and hydrocyanic acid are extremely weak. The consequence is that, as the reaction proceeds toward the right, there will be a large fall in the ammonium ions from the ionization of NH_4CN to that of NH_4OH. There will be a much larger fall in the concentration of the cyanide ion, due to the extreme weakness of HCN. Considering the reverse reaction, there will be a small fall in hydroxyl and hydrogen ion concentration toward the formation of water. Since both NH_4OH and HCN are weak, this decrease will be almost negligible as compared to the other two. The results are that the reaction goes almost to completion toward the right.

A salt of a weak acid and a weak base, then, is extensively hydrolyzed by water.

Equilibrium Shift by Formation of a Complex Ion. — *a. Complex Ions with Ammonia.* — We shall now consider a class of compounds which are of considerable importance in analytical work, both from the point of view of identifying elements as such, and of separating them from others.

If ammonium hydroxide is added to a solution of a copper salt, there is formed at first a blue precipitate of copper hydroxide. On further addition of ammonium hydroxide, however, the precipitate is dissolved and a deep-blue solution results. Obviously, the further addition of ammonium hydroxide causes an increase in OH^- concentration. It would therefore seem at first thought that instead of the $Cu(OH)_2$ dissolving, more of it would be precipitated.

On the basis of what we have just learned about amphoteric hydroxide, it might be thought that $Cu(OH)_2$ is a hydroxide of this type, and therefore capable of dissolving in excess ammonium hydroxide, as represented in the following:

$$\overset{++}{Cu} + 2\overset{-}{OH} \rightleftarrows Cu(OH)_2 \leftrightarrows \boxed{\begin{matrix} 2\overset{+}{H} \\ 2NH_4OH \rightleftarrows \\ 2\overset{-}{OH} \end{matrix}} \begin{matrix} CuO_2^{=} \\ \\ + 2\overset{+}{NH_4}. \end{matrix}$$

$$\boxed{\begin{matrix} 2\overset{+}{H} \\ 2\overset{-}{OH} \end{matrix}} \Rightarrow H_2O$$

Were this the truth, sodium hydroxide would dissolve the $Cu(OH)_2$ even more readily than NH_4OH. Actually it does nothing of the kind. Instead, NaOH precipitates $Cu(OH)_2$ completely.

We must, therefore, seek in another direction for the explanation of this peculiar phenomenon. The color-change from the light greenish blue of the Cu^{++} ion is an indication that a new compound is formed, probably containing a new ion.

In neutral or slightly acid solutions, ferrocyanides give a quite insoluble precipitate with the cupric ion. In the ammonia solution of a cupric salt considered above, no precipitate of cupric ferrocyanide is obtained. Obviously, there has been a very decided change in the concentration of the copper ion, for copper ferrocyanide is quite insoluble and gives a precipitate even with traces of copper.

Investigation has shown that a complex of copper ion and *ammonia* molecules of the composition $Cu(NH_3)_4^{++}$ is formed. This ion is deep blue in color and dissociated into Cu^{++} and $4NH_3$, but only to a very small extent, so small in fact, that, as stated above, copper ferrocyanide cannot be precipitated under ordinary conditions.

On the other hand, copper sulphide, which is ever so much more insoluble than the ferrocyanide, can be precipitated. This indicates that the complex $Cu(NH_3)_4^{++}$ is dissociated. The equation for its dissociation would be as follows:

$$Cu(NH_3)_4^{++} \rightleftarrows Cu^{++} + 4NH_3,$$

and the mass-action equation:

$$(1) \qquad \frac{[Cu^{++}] \times [NH_3]^4}{[Cu(NH_3)_4^{++}]} = K.$$

We are now in a position to explain the phenomenon of precipitating copper hydroxide with ammonia and its redissolving. Copper hydroxide is quite insoluble, and with the original concentration of Cu^{++} and OH^- ions from the cupric salt and ammonium hydroxide respectively, $Cu(OH)_2$ is precipitated. It can be seen, though, from equation 1 above, that, as the concentration of NH_3 increases, the concentration of Cu^{++} ion decreases as the fourth power. Since concentrated ammonia is only about 1 per cent ammonium hydroxide and 35 per cent dissolved ammonia gas, the concentration of NH_3 mounts pretty rapidly as ammonium hydroxide is added. This means a very rapid decrease in

Cu^{++} ion. As a consequence, the solution soon becomes undersaturated with respect to $Cu(OH)_2$ (**the S. P. Principle**), and it begins to dissolve, since:

$$[Cu^{++}] \times [OH^-]^2 = K_{sp}$$

for copper hydroxide must be satisfied. If the addition of ammonium hydroxide continues, all the $Cu(OH)_2$ will be dissolved and the blue color remains.

If an acid, say H_2SO_4, is added to this deep-blue solution until the solution is acid, the blue color disappears and the normal bluish green of the copper ion is restored. This can be explained as follows: The dissociation of the copper-ammonia complex is:

$$Cu(NH_3)_4 \rightleftarrows Cu^{++} + \boxed{4NH_3}$$

$$2H_2SO_4 \rightleftarrows 2SO_4^{=} + \boxed{4H^+}$$

$$\Downarrow$$

$$4NH_4^+.$$

The sulphuric acid, dissociating into hydrogen and sulphate ions as shown, offers the opportunity for the combination of the ammonia molecule and the hydrogen ion to form the ammonium ion. This equilibrium is practically 100 per cent in the direction of the ammonium ion, so that the ammonia molecules are completely removed from the solution if enough hydrogen ion is added. This means that $Cu(NH_3)_4^{++}$ will dissociate further to replace the lost NH_3, and in so doing will return Cu^{++} ions to the solution. In this way, if enough acid is added, all the Cu^{++} ions originally present will be returned, the $Cu(NH_3)_4^{++}$ complex will be destroyed, and the deep-blue color lost.

Beside copper, four other elements, silver, zinc, nickel, and cadmium, among the common metals as they occur in qualitative work, all form ammonia complexes of the same type. The number of ammonia molecules associated with the complex is always twice the valence of the metal, but

the valence of the whole complex is always the same as that of the metal. Thus we have:

$Cu(NH_3)_4^{++}$
$Cd(NH_3)_4^{++}$
$Ag(NH_3)_2^{+}$
$Zn(NH_3)_4^{++}$
$Ni(NH_3)_4^{++}$, etc.

All of these complexes are very weakly dissociated and consequently offer analytical advantages in detecting these metals. Thus, silver chloride may be dissolved away from lead and mercurous chlorides by ammonium hydroxide. The explanation of its solution is the same as that for copper hydroxide. The silver chloride may then be reprecipitated by means of nitric acid.

Another example is afforded in aluminium and zinc hydroxides, both of which are insoluble. The addition of ammonium hydroxide to a solution of aluminium and zinc ions precipitates aluminium hydroxide, which does not form a complex, but keeps the zinc in solution (since $Zn(NH_3)_4(OH)_2$ is not insoluble), and thus affects a separation.

$$AlCl_3 \rightleftarrows \boxed{Al^{+++}} + 3Cl^-$$

$$3NH_4OH \rightleftarrows \boxed{3OH} + 3NH_4^+$$

$$3NH_3 \quad 3H_2O \qquad \boxed{\quad} \qquad Al(OH)_3 \text{ (dissolved)}$$

$$Al(OH)_3 \text{ (solid)}$$

$$ZnCl_2 + 2NH_4OH \rightarrow Zn(OH)_2 \rightleftarrows \boxed{Zn^{++}} + 2OH^-$$

$$4NH_4OH \rightleftarrows \boxed{4NH_3} + 4H_2O$$

$$NH_4^+ \quad OH^- \qquad Zn(NH_3)_4^{++}$$

Equilibrium Shift by Formation of a Complex Ion. — *b. Complex Ions with Sulphur.* — Another very important class of complex ions are those formed by certain sulphides with the sulphide ion. Arsenic in both its valences, antimony in both its valences, tin in its higher valence, and bivalent mercury all have the ability to form complex sulphur anions.

Arsenic, antimony, and tin dissolve in both ammonium sulphide and ammonium polysulphide, as well as in sodium monosulphides and polysulphides, as a result of the formation of these complexes. Mercuric sulphide dissolves only in the sulphides of sodium.

As in the case of the complex ammonia ions, the complex sulphur ions are composed of a molecule and an ion, and are *very weakly dissociated.* Thus, for the solution of arsenious sulphide by either ammonium or sodium sulphide, the following equilibria are written:

$$\overset{\text{(solid)}}{As_2S_3} \rightleftarrows \boxed{As_2S_3} \overset{\text{(dissolved)}}{\rightleftarrows} 2As^{+++} + 3S^{=}$$

$$3(NH_4)_2S \rightleftarrows \boxed{3S^{=}} + 6NH_4^{+}.$$

$$\boxed{3S^{=}} \Updownarrow 2AsS_3^{\equiv}$$

The arsenious sulphide, though very insoluble, dissolves to a small extent and is ionized into trivalent As^{+++} and $S^{=}$ ions. The ammonium or sodium sulphide is ionized into the metallic ion and sulphur ion. The latter combines with the molecular As_2S_3 to form the **very weakly** ionized complex $AsS_3^{\equiv}$, thus undersaturating the solution with respect to As_2S_3. More of this dissolves to saturate the solution, but is immediately taken up by the sulphur ions. If enough ammonium or sodium sulphide is added, all the As_2S_3 can be dissolved.

The arsenious sulphide may be reprecipitated by the addi-

tion of hydrochloric acid. The explanation is as follows: From the equilibrium equation,

$$As_2S_3 + 3S^{=} \rightleftarrows 2AsS_3^{\equiv},$$

we may write

$$\frac{[As_2S_3] \times [S^{=}]^3}{[AsS_3^{\equiv}]^2} = K. \qquad (1)$$

From equation **1** it is clear that the greater the concentration of the $S^{=}$ ion, the greater will have to be the concentration of $AsS_3^{\equiv}$ to keep K constant. As acid is added and the H^{+} ion is increased, the $S^{=}$ is rapidly decreased, as is evident from the equation for hydrogen sulphide:

$$\frac{[H^{+}]^2 \times [S^{=}]}{[H_2S]} = K. \qquad (2)$$

From equation **1** it can be seen that, as $[S^{=}]$ decreases, $[As_2S_3]$ must increase and $[AsS_3^{\equiv}]$ decrease to keep K constant. When this change becomes sufficiently great to saturate the solution with As_2S_3, the latter begins to precipitate and will be completely precipitated if enough acid is added.

The complex ions * of the other valence of arsenic, and of antimony, tin, and mercury, are of the same character and formed in the same way (remembering that HgS is soluble only in sulphides of sodium). The equilibria may be written as follows:

* The student frequently has difficulty in remembering the formulas of the complex salts of arsenic, antimony, and tin. If for the former two he remembers that they are just below phosphorus in the same group in the periodic table, and form analogous compounds, he will have no trouble. He knows that phosphoric acid is H_3PO_4; substituting As or Sb for P, he has H_3AsO_4 or H_3SbO_4; again, substituting divalent S for divalent O, and monovalent NH_4 or Na for monovalent H, gives Na_3AsS_4 or $(NH_4)_3SbS_4$ as the case may be.

For tin, he need but remember that it is in the fourth group with carbon and forms an acid, H_2SnO_3, analogous to H_2CO_3. The substitutions are made as above.

(1)

(solid)	(dissolved)	(ionic)
$As_2S_5 \rightleftarrows$	As_2S_5	$\rightleftarrows 2As^{+++++} + 5S^{=}$
$3Na_2S \rightleftarrows$	$3S^{=}$	$+ 6Na^{+}$

$\updownarrow$

$2AsS_4^{\equiv}$ (weak complex)

(2)

(solid)	(dissolved)	(ionic)
$Sb_2S_3 \rightleftarrows$	Sb_2S_3	$\rightleftarrows 2Sb^{+++}\ 3S^{=}$
$3Na_2S \rightleftarrows$	$3S^{=}$	$6Na^{+}$

(weak complex) $2SbS_3^{\equiv}$ $\updownarrow$

(3)

(solid)	(dissolved)	(ionic)
$Sb_2S_5 \rightleftarrows$	Sb_2S_5	$\rightleftarrows 2Sb^{+++++}\ 5S^{=}$
$3Na_2S \rightleftarrows$	$3S^{=}$	$+ 6Na^{+}$

$\updownarrow$

$SbS_4^{\equiv}$ (weak complex)

(4)

(solid)	(dissolved)	(ionic)
$SnS_2 \rightleftarrows$	SnS_2	$\rightleftarrows Sn^{++++} + 2S^{=}$
$Na_2S \rightleftarrows$	$S^{=}$	$+ 2Na^{+}$

$\updownarrow$

$SnS_3^{=}$ (weak complex)

(5)

(solid)	(dissolved)	(ionic)
$HgS \rightleftarrows$	HgS	$\rightleftarrows Hg^{++} + S^{=}$
$Na_2S \rightleftarrows$	$S^{=}$	$+ 2Na^{+}$

$\updownarrow$

$HgS_2^{=}$ (weak complex)

It will be noted that, in all the above illustrations, only the monosulphide of sodium or ammonium is considered, whereas in most procedures, the polysulphide of either is used. The necessity for polysulphide is due to divalent tin, which forms no complex. The extra sulphur atoms in the polysulphides act as oxidizing agents and oxidize the tin to its higher valence. The higher sulphide of tin then dissolves as shown. The equation may be written:

$$\begin{array}{rcl} SnS + S^{=} \rightarrow & \boxed{SnS_2} & \rightleftarrows SnS_3^{=} \text{ (weak complex)} \\ \uparrow & & \\ Na_2S_x \rightleftarrows & \boxed{S^{=}} & 2Na^{+}. \end{array}$$

As in the case of tin, the lower sulphides of arsenic and antimony are also oxidized (really sulphurized) to the higher sulphides, which in turn dissolve to give the higher sulphosalts, as shown:

$$\begin{array}{rcl} As_2S_3 + 2S^{=} \longrightarrow & \boxed{As_2S_5} & \rightleftarrows AsS_4^{\equiv} \\ \uparrow & & \\ 3Na_2S_x \rightarrow & \boxed{3S^{=}} & 6Na^{+}. \end{array}$$

The same may be written for antimony, though of course not for mercury, since mercury has no higher valence.

Equilibrium Shift by Formation of a Complex Ion. — *c. The Action of Arsenic Acid with Hydrogen Sulphide.* — Though the action of arsenic acid toward H_2S does not particularly involve any complex ion, it is included here because of its importance in connection with the analysis of this group. In precipitating the arsenic-copper group of elements, the acid concentration should be adjusted to definite strengths for the best results. Since the acid concentration in the original is generally unknown, the solution is evaporated to dryness and 30 milli-equivalents (2.5 c.c.) of concentrated

hydrochloric acid are added. If during the evaporation trivalent arsenic and chlorides are present, there is danger of loss of arsenic, since arsenious chloride boils at 130.2°. To overcome this, a few drops of nitric acid are added. This oxidizes the arsenic to arsenic acid (pentavalent arsenic).

$$(AsCl_3 + 3H_2O \rightleftarrows As(OH)_3 + 3HCl) \times 6$$
$$(2As(OH)_3 \rightarrow As_2O_3 + H_2O) \times 3$$
$$(2HNO_3 \rightarrow H_2O + 2NO + 3O) \times 2$$
$$(As_2O_3 + 2O \rightarrow As_2O_5) \times 3$$
$$(H_2O + As_2O_5 \rightarrow 2H_3AsO_4) \times 3$$

This shows only the conversion of the arsenic chloride to arsenic acid, in which the arsenic goes to the pentavalent form. No consideration of the oxidation of HCl, etc., is given, since it does not affect the arsenic.

Arsenious acid, $As(OH)_3$, as previously pointed out, is decidedly amphoteric. Its dissociation into As^{+++} and OH^- ions is easily sufficient to cause rapid precipitation of As_2S_3. Arsenic acid, H_3AsO_4, is very similar to phosphoric acid. It is moderately dissociated as follows:

$$H_3AsO_4 \rightleftarrows H^+ + H_2AsO_4^- \rightleftarrows 2H^+ + HAsO_4^{=} \rightleftarrows 3H^+ + AsO_4^{\equiv}.$$

The secondary and tertiary ionizations of arsenic acid are very weak, as with phosphoric, but the primary ionization is about 27 per cent. The basic tendencies of arsenic acid are practically nil. Thus when we try to precipitate arsenic sulphide from H_3AsO_4 under normal conditions, it precipitates very slowly because there is no As^{5+} ion available to form As_2S_5, except from an extremely small dissociation of arsenic acid, as follows:

$$H_3AsO_4 + H_2O \rightleftarrows \overset{++}{As}^{+++} + 5OH^-.$$

The arsenic sulphide in a 0.3 normal solution of HCl may take as long as twenty-four hours to be completely pre-

cipitated in the cold. The action which takes place has not been completely explained, but probably is a combination of two functions as indicated in the following equations:

(1) $2H_3AsO_4 + 5H_2S \rightarrow As_2S_5 + 8H_2O$

and

(2) $2 \times (H_3AsO_4 + H_2S \rightarrow H_3AsO_3S + H_2O)$

(3) $2 \times (H_3AsO_3S \rightarrow H_3AsO_3 + S)$

(4) $2H_3AsO_3 + 6HCl \rightarrow 2AsCl_3 + 6H_2O$

(5) $2AsCl_3 + 3H_2S \rightarrow As_2S_3 + 6HCl.$

There are really two separate actions: in equation **1**, the direct precipitation of arsenic as As_2S_5; and in equations **2**, **3**, **4**, and **5**, the reduction of the arsenic acid to arsenious acid through the formation of the fairly stable monosulph-arsenic acid, H_3AsO_3S. The arsenic from this compound is then precipitated in the trivalent form as the equations indicate. As stated above, in cold dilute solutions of HCl, this action goes on very slowly. It has been found, however, that heat and a high concentration of HCl (2.5 c.c. concentrated HCl in a total volume of 5 c.c.) cause rapid precipitation of the arsenic. This is probably due to the facts (1) that the H_3AsO_3S is unstable in the presence of concentrated HCl, especially when heated; and (2) that H_3AsO_4 is partially converted into $AsCl_5$ as follows:

$$H_3AsO_4 + 5HCl \rightleftarrows AsCl_5 + 4H_2O,$$

when the HCl is sufficiently concentrated.

Since high concentrations of acid would seriously interfere with the successful precipitation of some of the other sulphides of the copper-arsenic group (cadmium sulphide, for example), it is advisable after evaporation to add 2.5 c.c. of concentrated HCl, dilute to 5 or 8 c.c., heat almost to boiling, and pass in a rapid stream of H_2S. After five minutes the arsenic may be considered completely precipitated and

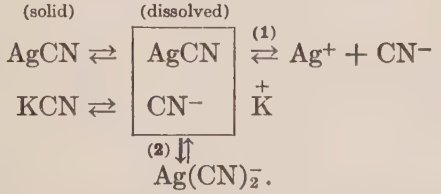
the solution diluted to such volumes as will permit the complete precipitation of the other metals of the group.

Equilibrium Shift by Formation of a Complex Ion. — *d. Other Complex Ions.* — Among several other types of complex ions which may be formed, the most important are those with the CN^- radical. Gold, silver, mercury, copper, cadmium, cobalt, nickel, and iron, among others, all have the ability to form complex cyanides of the same type. All of them are quite stable. Thus, for example, if potassium cyanide is added to a solution of a silver salt, a very insoluble precipitate of AgCN is formed, but it dissolves in an excess of the potassium salt. This may be written:

$$KCN + AgNO_3 \rightarrow AgCN + KNO_3$$

$$AgCN + KCN \rightarrow KAg(CN)_2.$$

The type of action is the same here as in other complex-ion formations: the combination of an ion (CN^-) with a molecule (AgCN) to form a very weakly ionized complex ($Ag(CN_2)^-$). The equation may be written:



The silver has gone entirely into the negative side of the compound. That this is true can be shown by electrolysis, which causes all but traces of the silver to move toward the positive pole.

The complex $Ag(CN)_2^-$ is a very stable one, so stable that the addition of a chloride will *not* precipitate silver chloride. Since silver chloride is quite insoluble, the concentration of the silver ion must be very low in order not to precipitate.

The concentration of the silver ion depends on the concentration of the cyanide ion, according to the equations:

(a) (from **2** above) $$\frac{[AgCN] \times [CN^-]}{[Ag(CN)_2^-]} = K$$

(b) (from **1** above) $$\frac{[Ag^+] \times [CN^-]}{[AgCN]} = K';$$

multiplying **a** by **b**,

$$\frac{[Ag^+] \times [CN^-]^2}{[Ag(CN)_2^-]} = K''.$$

If, therefore, an excess of KCN is added, the concentration of the silver ion is cut down as the cyanide ion concentration increases. Furthermore, it is lowered in proportion to the square of the cyanide ion concentration. Thus, by addition of a comparatively small excess of KCN, the silver ion concentration can be so reduced that silver sulphide cannot be precipitated from the solution. Silver sulphide is one of the most insoluble compounds we know; its $K_{sp} = 4 \times 10^{-50}$ and the concentration of silver ion necessary to precipitate it from its saturated solution is about 1.6×10^{-17}, a concentration many billion times smaller than the H^+ ion in water. The concentration of silver ion in the presence of excess potassium cyanide, then, is almost zero for all practical purposes.

The relationships which have been discussed for the complex cyanide of silver hold in greater or less degree for all the other complexes. Since, owing to the exceedingly poisonous character of potassium cyanide, most procedures avoid its use, individual discussion of each will be dispensed with. The equations for the formation of the more important complex cyanides, however, are given herewith:

(1) $$HgCl_2 + 2KCN \rightarrow Hg(CN)_2 + 2KCl$$

$$Hg(CN)_2 + 2KCN \rightarrow K_2Hg(CN)_4$$

(2) $CuCl + KCN \rightarrow CuCN + KCl$

$CuCN + 2KCN \rightarrow K_2Cu(CN)_3$.

(Cupric salts are reduced to cuprous by KCN, and the complex is then formed.)

(3) $CdCl_2 + 2KCl \rightarrow Cd(CN)_2 + 2KCl$

$Cd(CN)_2 + 2KCN \rightarrow K_2Cd(CN)_4$

(4) $FeCl_2 + 2KCN \rightarrow Fe(CN)_2 + 2KCl$

$Fe(CN)_2 + 4KCN \rightarrow K_4Fe(CN)_6$

(5) $FeCl_3 + 3KCN \rightarrow Fe(CN)_3 + 3KCl$

$Fe(CN)_3 + 3KCN \rightarrow K_3Fe(CN)_6$.

The latter two — the ferrocyanides and ferricyanides — are the most familiar of the complexes. They are both very stable; if to a solution of $K_3Fe(CN)_6$ some thiocyanate is added, no trace of red color is shown. When one considers that the thiocyanate test for ferric iron is a very delicate one, the above gives evidence that the ferricyanide ion is very little dissociated.

Summary of Complex-Ion Formation. — From the foregoing we have seen that complex ions have the following properties:

1. Formed from a molecule and an ion
2. Very stable in general, i.e., weakly dissociated.

From the latter property it is obvious that when the components of a complex ion are present, there will be a strong tendency toward its formation, and a consequent equilibrium shift in the direction of the complex.

Equilibrium Shift by Change in the Charge of an Ion (Oxidation and Reduction). — Though the change in charge on an ion is not used very frequently for the express purpose

of bringing about an equilibrium shift, yet this type of reaction (oxidation and reduction) occurs very often and is therefore important.

The term *oxidation*, being naturally associated with the name *oxygen*, from whence it originated, is misleading. In the present-day understanding, it does not necessarily involve oxygen. In the early history of chemistry, most of the reactions of this type involved oxygen; they were consequently classed by themselves and called *oxidation reactions*. This class has been broadened to involve many reactions of similar nature which do not involve oxygen at all. So, for example, both of the following reactions are considered oxidations:

$$2Cu + O_2 \rightarrow 2CuO$$

$$Cu + S \rightarrow CuS.$$

Similarly for such a change as takes place with iron compounds; ferrous oxide on oxidation gives ferric oxide, yet ferric chloride bears the same relation to ferrous chloride as the higher oxide does to the lower. The change of ferrous chloride to ferric is therefore considered an oxidation.

On examining many changes of this type, it becomes apparent that the common factor is valence change. Whenever we speak of an oxidation's having taken place, we note that the number of positive valences of an element has been increased. We define oxidation therefore as follows: **Oxidation is the increase in the number of positive charges of an element.**

The opposite of oxidation would be an increase in the number of negative charges; this is called *reduction:* **Reduction is the increase in the number of negative charges of an element.**

We shall see later that wherever the *positive* valence of one element is increased, of necessity the *negative* valence of some other element involved in that reaction is also increased.

In other words, oxidation and reduction always occur together; whenever one element is oxidized, some other element is reduced. Thus in the case of the union of sulphur with copper, both are originally of zero valence; but when they unite, the copper shows two positive charges and the sulphide two negative charges. The former has been oxidized and the latter reduced.

Electrons and Change of Valence. — From what we know of the electronic structure of atoms and the fact that their valence is due to an excess of either protons or electrons, we can readily interpret the meaning of the changes in valence which take place in oxidation and reduction reactions. When a given element is oxidized and another is simultaneously reduced, it simply means that the former has had electrons removed from its valence orbit and that in consequence a larger number of excess protons is now present. Contrary to the old idea of thinking of oxidation as a gain in positive charges by an element, we see that there is really no gain but a loss in negative charges. This loss in negative charges is taken up by the element reduced. We should keep well in mind, however, that all changes in valence are brought about by addition or subtraction of electrons from the elements and never by any change in the number of protons.

We may now look at and define oxidation and reduction in a different, simpler manner: **Oxidation is the removal of electrons from an element; reduction is the addition of electrons to the element.** So when copper unites with oxygen,

$$2\,Cu + O_2 \rightarrow 2\,CuO,$$

each atom of copper loses two electrons and has in excess then two protons, or a positive valence of two; each atom of oxygen gains the two electrons lost by the copper and has two excess negative charges, or a negative valence of two. The copper has been oxidized and the oxygen reduced.

To take a somewhat more complex case, consider the reduction of mercuric chloride by stannous chloride:

$$2HgCl_2 + SnCl_2 \rightarrow 2HgCl + SnCl_4.$$

Each mercury atom gains one electron, and so is reduced. Each tin atom gives up two electrons, one to each mercury atom. The tin is oxidized from a valence of two to a valence of four.

Writing Equations for Oxidation and Reduction Reactions. — Most of the reactions involved in analytical chemistry are double decompositions. If the student learns the valences of the metals and the acid radicals, he is in a position to write the formula for any compound involved in his work. Knowing the formulas involved in a reaction where double decomposition takes place is all that is necessary for writing the equation, because the balancing of such equations is, almost invariably, quite simple.

Such equations as are not double decompositions are almost always oxidation and reduction reactions. Unfortunately for the student, they are not always simple, and no simple systematic process is applicable to their solution. The result is that the student attempts to memorize such equations. Even if he is successful in learning all of them well, his retention of them is only temporary.

With comparatively little practice and thought, the student can gain command of the following method of writing such equations. This method is systematic in principle and generally applicable though the student should not get the idea that all he need know about an equation is this method of solution and the chemicals used. We can, after all, write several equations for the reaction of a given set of chemicals. Under given conditions, only one of these, in general, will be correct. The student should, therefore, in learning an

equation, first learn (1) **what chemicals are used, and** (2) **what products are formed.***

The student almost invariably objects, saying that if he is to memorize this much he may as well remember the numbers too. Actually, though, the reactions of most of the oxidizing and reducing agents are typical, so that, with a little practice, the student can predict what the products formed will be, and need not memorize them for each individual case. So, for example, when potassium permanganate acts as an oxidizing agent, it almost invariably is used in acid solution. The manganese under these circumstances gains five electrons, going from a valence of seven to a valence of two ($Mn^{(7+)} \rightarrow Mn^{++}$). Heptavalent manganese always appears as part of a permanganate acid radical, divalent manganese always as a manganous basic radical. The five charges must be taken up by the substance oxidized, and the products formed as a result must be remembered. So far as the manganese is concerned, however, the same action always takes place.

$$Mn^{(7+)} \rightarrow Mn^{++}.$$

What the acid radical which unites with manganese will be depends upon the acid or acids used in the reaction. This will be illustrated later.

Another common oxidizing agent is potassium dichromate in acid solution. Under these conditions, the chromium goes from the hexavalent condition in the acid radical to trivalent chromium as a metallic radical.

$$Cr_2^{(6+)}O_7 \rightarrow 2Cr^{+++}.$$

* When a student is in any doubt whatever as to the products of an oxidation, he should immediately consult a text for the facts. Any guess may be entirely wrong. Too much emphasis cannot be placed upon the indispensable fact that we *must* know the reactants and the resultants to write an equation. There is no formula which will tell these.

Again, the salt formed by the trivalent chromium depends on the acid used.

The first step in writing oxidation and reduction equations is to be able to tell the valence of the element which is to be oxidized or reduced. How, for example, do we know that Mn has a valence of 7 in $KMnO_4$? that Cr is 6 in $K_2Cr_2O_7$? The process for determining this is simple. **First of all, the sum of the positive and negative valences in any compound must equal zero.** The student should know that (with a few exceptions which do not enter elementary considerations) oxygen has a negative valence of two, and hydrogen a positive valence of one. If he knows the positive valences of the common metals, the rest is easy.

Let us take $KMnO_4$. There are four oxygens, which means eight negative valences. There is one potassium, giving one positive valence.

$$\begin{aligned} 4O &= 4 \times (-2) = -8 \\ 1K &= 1 \times \quad (1) = \quad 1 \\ &\text{Difference} \quad -7 \end{aligned}$$

The difference between these two is the number of valences which one atom of manganese must have to make this compound electrically neutral. Obviously this is plus seven $(+7)$; the valence of Mn in $KMnO_4$.

Let us try $K_2Cr_2O_7$. Here we have seven oxygens, giving fourteen negative valences and two positive potassium valences.

$$\begin{aligned} 7O &= 7 \times (-2) = -14 \\ 2K &= 2 \times (\quad 1) = \quad 2 \\ &\text{Difference} \quad -12 \end{aligned}$$

The difference is twelve negative valences to be accounted for by two chromium atoms. Each chromium must therefore be $(+6)$.

The next step is to remember that, in an equation, just as in a compound, the sum of all the positive and negative

valences is equal to zero. **Therefore, if some element loses a given number of charges, that same number must be gained by one or more of the other elements.** So when Mn goes from a valence of (+ 7) to a valence of (+ 2), some other element or elements involved in the reaction must acquire (+ 5) charges, or, to be more accurate, lose five electrons (which are gained by the manganese).

Lastly, we must remember that all free elements have a zero valence. There is no excess or lack of electrons, and therefore no positive or negative charge.

Let us take a balanced equation to show how these ideas apply:

$$K_2Cr_2O_7 + 14HCl \rightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2.$$

Determining the valence of Cr in $K_2Cr_2O_7$ as above, we see that it is six, and that it is reduced to three in $CrCl_3$. Since there are two chromium atoms each losing three positive (3 +) charges, some other element or elements must gain these six positive charges (actually, lose six electrons). In this case the six chlorine atoms on the right-hand side of the equation are zero-valent, being the free element. All of the chlorine atoms on the left side of the equation have a negative valence of one (− 1). Each of the six on the right-hand side must have gained a positive charge (lost one electron) to become zero-valent, thus accounting for the six positive charges lost by the two chromium atoms.

The Ion-Electron Method of Writing Oxidation and Reduction Equations. — In the reaction above and all others, it will be noted that certain of the elements are not involved in the breakdown of the oxidizing agent. Thus the two potassium atoms in potassium dichromate and the six chlorine atoms which go to the two trivalent chromium atoms are not particularly involved in the oxidation and reduction. For the sake of simplicity, these may be omitted

from the preliminary writing of an equation. Thus the reaction may be written:

$$Cr_2^{(6+)}O_7^{=} + H^+ + Cl^- \rightarrow 2Cr^{+++} + Cl^0 + 7H_2O.$$

In the above statement lies the foundation of what happens in the reaction. This may be subdivided again into (1) what happens in the oxidizing agent and (2) what happens to the substance oxidized.

Considering the former, the two chromium atoms of the oxidizing agent $Cr_2O_7^{=}$ go to form $2Cr^{+++}$ and all the oxygen forms water, using $14H^+$:

(1) $$Cr_2^{(6+)}O_7^{=} + 14H^+ \rightarrow 2Cr^{+++} + 7H_2O.$$

So far as the atoms of the elements are concerned, the equation is balanced, but when we total the positive and negative charges, we see that there is a deficiency of twelve positive charges on the left-hand side of the equation and six negative charges on the right-hand side. The difference being six, we may write:

$$Cr_2^{(6+)}O_7^{=} + 14H^+ + 6(-) \rightarrow 2Cr^{+++} + 7H_2O.$$

Considering now the reducing agent, the change from Cl^- to Cl_2 may be written:

(2) $$2Cl^- \rightarrow Cl_2^0.$$

There is a deficiency of two negative charges on the right-hand side, so we write:

$$2Cl^- \rightarrow Cl_2^0 + 2(-).$$

To balance equation **2** with equation **1** necessitates multiplying the former by 3. Doing this and adding the two, we have:

$$Cr_2^{(6+)}O_7^{=} + 14H^+ + 6Cl^- \rightarrow 2Cr^{+++} + 7H_2O + 3Cl_2.$$

This equation is the same as

$$K_2Cr_2O_7 + 14HCl \rightarrow 2CrCl_3 + 2KCl + 7H_2O + 3Cl_2,$$

except that the two potassium ions and two chromium ions are not taken care of. Since both are positive, and there are no other negative ions left but eight of chlorine, the compounds formed are $2KCl$ and $2CrCl_3$.

For the sake of completeness, let us consider the more complicated case of oxidation of hydrogen sulphide by potassium permanganate in sulphuric acid solution. Obviously, the oxidizing agent is the permanganate; the reducing agent, hydrogen sulphide. We must know the following:

1. Mn in acid solution of $KMnO_4$ forms Mn^{++} on reduction.
2. Free sulphur is formed, which means $S^{=} \rightarrow S^0$.

We may write:

$$Mn^{(7+)}O_4^- + H^+ + S^{=} \rightarrow H_2O + Mn^{++} + S^0.$$

Considering what happens to the MnO_4^- ion (the oxidizer), we write:

(1) $$Mn^{(7+)}O_4^- + 8H^+ \rightarrow Mn^{++} + 4H_2O.$$

When we total the positive and negative charges, there is a deficiency of five negative charges $(5-)$ on the left-hand side. We have then:

(2) $$Mn^{(7+)}O_4^- + 8H^+ + 5(-) \rightarrow Mn^{++} + 4H_2O.$$

Considering the reducing agent,

(3) $$S^{=} \rightarrow S^0,$$

there is a deficiency of two negative charges on the right side of the equation. We should write:

(4) $$S^{=} \rightarrow S^0 + 2(-).$$

To balance **2** and **4**, we multiply **2** by 2 and **4** by 5. Adding the result, we have:

$$2Mn^{(7+)}O_4^- + 16H^+ + 5S^{=} \rightarrow 5S^0 + 2Mn^{++} + 8H_2O.$$

Since the acid used was sulphuric, the only acid radicals available for the $2\,Mn^{++}$ and the $2K^+$ are $SO_4^{=}$ radicals. The $2\,Mn^{++}$ and $2K^+$ require $3\,SO_4^{=}$ radicals, using up

$6H^+$. The other $10H^+$ go to the $5S^=$ to form the H_2S. The complete equation is:

$$2KMnO_4+3H_2SO_4+5H_2S \rightarrow 2MnSO_4 + K_2SO_4 + 8H_2O+5S.$$

Equilibrium Shift by Means of Oxidation and Reduction Actions. — As stated in the beginning of this discussion, it is not frequent that a shift of equilibrium is brought about by oxidation and reduction. There are, however, a few important cases. Silver sulphide dissolves in nitric acid, for example, whereas it will not dissolve in hydrochloric. At first sight it would seem that it might dissolve in either:

(1)

$$\underset{\text{(solid)}}{Ag_2S} \rightleftarrows \underset{\text{(dissolved)}}{Ag_2S} \rightleftarrows \underset{\text{(ionic)}}{2Ag^+ + S^=}$$

$$HCl \rightleftarrows Cl^- + 2H^+$$

$$\uparrow\downarrow$$

$$H_2S$$

In this equation, if we proceed to look for the weak compound, H_2S answers and, in keeping with our ideas, **is actually formed,** but in **very small quantity.** It so happens, however, that Ag_2S is extremely insoluble ($K_sP = 4.0 \times 10^{-50}$), and the very small concentration of $S^=$ ions from the little H_2S formed is sufficient to exceed the K_{sp} for silver sulphide. In other words, an equilibrium is established as shown in **1**, but the reaction is practically entirely toward the left (←).

In the case of HNO_3, the same set of circumstances prevails as long as the solution is cold and dilute. If the mixture is heated, the HNO_3 functions not only to form H_2S, but to oxidize the $S^=$ to free sulphur and thereby destroy it.

(2)

$$\underset{\text{(solid)}}{Ag_2S} \rightleftarrows \underset{\text{(dissolved)}}{Ag_2S} \rightleftarrows \underset{\text{(ionic)}}{2Ag^+ + S^=} \rightarrow S^0 \text{ (oxidized by } HNO_3\text{)}$$

$$HNO_3 \rightarrow 2NO_3^- + 2H^+$$

$$\uparrow\downarrow$$

$$H_2S$$

Since $S^=$ ions are destroyed, the equilibrium **b** is disturbed and more dissolved Ag_2S goes into the ionic form. As a result of this, more solid dissolves. Continued oxidation will cause a complete solution of Ag_2S.

We have then a reduction of the concentration of the $S^=$ ions practically to zero and consequent equilibrium shift by means of an oxidation reaction.

The same type of reasoning applies to the rapid solution of cobalt and nickel sulphides in *aqua regia*. Both these sulphides dissolve only very slowly in hydrochloric acid.

SUMMARY

We have just learned that:

1. In attempting ionic explanations in analytical chemistry we must keep two things in mind. They are:
   (a) formation of a weak electrolyte, and
   (b) the solubility product principle.
2. We should try to apply the former in any case and the latter to such cases as involve a precipitate.
3. The shift of ionic equilibria may be brought about in several ways. They are:
   (a) formation of an insoluble compound,
   (b) addition of a common ion,
   (c) formation of a slightly ionized compound,
   (d) formation of a complex ion, and
   (e) oxidation and reduction.
4. An *amphoteric hydroxide* is one which at all times ionizes both as an acid and as a base.
5. *Hydrolysis* is a double decomposition in which water is one of the reactants. It is the reverse of neutralization.
6. The salt of a strong base and a weak acid reacts basic in solution. The salt of a strong acid and a weak base reacts acid in solution.

7. The ionization of water, though extremely small, is the prime factor in hydrolysis.
8. A complex ion is generally formed from a compound and an ion and is weakly dissociated.
9. *Oxidation* is the removal of electrons from an atom and *reduction* is the addition of electrons to an atom.

QUESTIONS

(*N.B.* — Questions on the application of principles to actual cases will be reserved for Chapter VIII, which is devoted exclusively to such questions.)

1. What are the two big factors to keep in mind when trying to explain a given phenomenon in analytical chemistry?
2. Do both of these factors always apply? Name some cases which illustrate your answer.
3. Name and illustrate all the different ways by means of which an ionic equilibrium may be shifted in one direction or the other.
4. Write a definition of hydrolysis and give several typical cases to illustrate.
5. Which of the following compounds would you expect to react basic, which acid? Give reasons for your answers, and illustrate by writing the ionic equations in diagram form: Na_2S, $AlCl_3$, Na_2CO_3, $BiCl_3$, $Na_2B_4O_7$.
6. In what type of compound would you expect hydrolysis to go to completion? Give a typical compound and explain its action.
7. What is meant by a *complex ion?* Give several examples found in qualitative analysis. Explain how their properties are put to use in the procedure.
8. What is meant by an *amphoteric hydroxide?* Name two such and show their use in the procedure.
9. Define oxidation and reduction in terms of valence change; in terms of electronic change.
10. Select several oxidation and reduction reactions which occur in your procedure and write equations for them by use of the ion-electron method.
11. Give an illustration of how an oxidation and reduction reaction is used to bring about a shift in an ionic equilibrium.

CHAPTER VII

SOME TYPICAL QUESTIONS AND ANSWERS

With a view toward giving the student some definite idea as to the general method of attack in answering questions involving theory in analytical work, some typical questions and their answers will now be given in full.

To be prepared to answer questions satisfactorily, the student is advised to use the following general method of attack:

1. **Know the table of ionizations of the common acids, bases, and salts.**
2. **Write the equilibrium equations for the compounds involved.**
3. **Look for a weakly ionized compound.**
4. **If a precipitate is formed, apply the Solubility Product Principle.**

In the following questions and answers, it will be noted (and pointed out) how generally the above procedure is followed. Truly enough, it is not a general formula for all cases; in fact there are incidents in which it might be misleading, but for most cases this method of procedure works admirably.

1. Question. — Explain, on the basis of the theory of ionization, why calcium carbonate dissolves in acetic acid.

Answer. — A precipitate of calcium carbonate sets up the following equilibria:

(1) $CaCO_3 \rightleftarrows CaCO_3 \rightleftarrows Ca^{++} + \boxed{CO_3^{=}}$

(2) $2HC_2H_3O_2 \rightleftarrows 2C_2H_3O_2^{-} \boxed{2H^{+}}$

$$\Updownarrow$$

$$H_2CO_3 \rightarrow H_2O + CO_2.$$

Acetic acid ionizes as shown. Examination for a weak compound shows two possibilities, calcium acetate and carbonic acid. The former, being a salt, is probably highly ionized; the latter, if we recall our table, is weakly ionized. H_2CO_3, then, is our **weak compound.** By its formation, $CO_3^{=}$ and H^+ ions are removed from the solution. The solution was saturated with $CaCO_3$:

$$[Ca^{++}] \times [CO_3^{=}] = K_{sp},$$

but removal of $CO_3^{=}$ ions has caused a fall in $[CO_3^{=}]$, so that the solution is undersaturated. (Here we have the application of the **Solubility Product Principle.**) As a result, equilibrium **2** shifts toward the right to reëstablish itself and restore the value $[Ca^{++}] \times [CO_3^{=}] = K_{S.P.}$ Thereupon, equilibrium **1** shifts in the same direction to replace the $CaCO_3$ (dissolved). In this manner, some of the $CaCO_3$ (solid) is dissolved. Addition of sufficient acid will result in complete solution of the $CaCO_3$. The action toward the right in this particular case is materially assisted by the fact that the molecular H_2CO_3, as it is formed, breaks down to form CO_2 and H_2O, thus preventing redissociation to $2H^+$ and $CO_3^{=}$.

Another Explanation. — The explanation of the solution of the carbonate may be approached in another manner. Considering the equilibrium for carbonic acid which is set up in the solution, we have:

$$\frac{[H^+]^2 \times [CO_3^{=}]}{[H_2CO_3]} = K$$

As the acetic acid is increased, the $[H^+]$ increases. The result is that $[CO_3^{=}]$ must decrease as the square of $[H^+]$, to keep K constant. $[CO_3^{=}]$ therefore becomes so low that:

$$[Ca^{++}] \times [CO_3^{=}] < K_{sp},$$

and both equilibria shift as previously explained.

It becomes obvious that any acid which gives an $[H^+]$ which is appreciably greater than the $[H^+]$ of H_2CO_3 will dissolve a carbonate.

If we choose a compound the acid radical of which comes from an acid of greater strength than the acid added, the compound will not dissolve. Thus, since calcium oxalate is a salt of oxalic acid, and the latter is a stronger acid by far than acetic, the oxalate will not dissolve in acetic acid, for

$$\frac{[H^+]^2 \times [C_2O_4^=]}{[H_2C_2O_4]} = K$$

is the equilibrium equation for $H_2C_2O_4$. Addition of acetic acid to this does not increase $[H^+]$. Therefore, there is no repression of the $[C_2O_4^=]$, and no tendency for CaC_2O_4 to dissolve. Addition of HCl, an acid whose $[H^+]$ is much greater than that of $H_2C_2O_4$, causes CaC_2O_4 to dissolve in the same way as $HC_2H_3O_2$ dissolves $CaCO_3$.

The solution of precipitates in acids in this way is quite general. Thus all the sulphides of the cobalt-iron group may be dissolved in dilute HCl (CoS and NiS very slowly); the insoluble phosphates, borates, nitrites, and chromates all dissolve in dilute solutions of a strong acid such as HCl. Many of these dissolve in as weak an acid as acetic, though not all. Thus the phosphates of barium, strontium, calcium, and magnesium, all dissolve in acetic acid, but those of iron, chromium, and aluminium are so insoluble that the reduction of $PO_4^=$ ion by addition of acetic acid is not sufficient to go below the solubility product of these three phosphates.

Co-Fe Group. — The student must be careful of the type of pitfall described above. A hasty application of the principle of the formation of a weak compound may lead to entirely erroneous results. Thus, for example, it would seem, from what is true of the sulphides of the cobalt-iron group, that the sulphides of the copper-tin group would also dissolve in dilute HCl. This is not the fact. Let us see if we

can explain why. Taking PbS as an example, the following equilibria are established:

$$PbS \rightleftarrows PbS \rightleftarrows Pb^{++} + \boxed{S^{=}}$$

$$HCl \rightleftarrows 2Cl^{-} + \boxed{2H^{+}}$$

$$\Downarrow$$

$$H_2S.$$

It would seem from this that the **weak compound** H_2S forms, and as a result, the PbS should dissolve as explained for calcium carbonate. The H_2S does form, but even so the $S^{=}$ ions removed from the solution are not sufficient to go below the solubility product of PbS, because the latter is so insoluble (S. P. $= 4.2 \times 10^{-28}$). The result is that lead sulphide is not dissolved by dilute HCl. Herein lies the basis of the separation of the copper-tin group from the cobalt-iron group. The solubility product constants of the former are so low that a concentration of HCl as high as $0.4N$ does not prevent their precipitation as sulphides, whereas the constants for the cobalt-iron group are sufficiently large to prevent sulphide precipitation except in very dilute acid solution.*

Effect of Alkaline Solution on Sulphide [$S^{=}$] Concentration.—To overcome the repressing effect of the H^{+} ion and thus permit precipitation of the cobalt-iron group, the solution is made alkaline with ammonium hydroxide. This destroys the H^{+} ion and at first sight just seems to give the full benefit of the $S^{=}$ ion concentration from H_2S. But it does more than this. Since H_2S is a very weak acid, its sulphide ion concentration in saturated solution is very low (1.2×10^{-15}). When it is passed into ammonium hydroxide, however, it is neutralized:

$$2NH_4OH + H_2S \rightleftarrows (NH_4)_2S + H_2O,$$

also $(NH_4OH + H_2S \rightleftarrows NH_4HS + H_2O)$.

* See also calculations for PbS and ZnS, Ch. I, pp. 108–110.

(The latter equation is omitted from consideration because the main effects come from the sulphide ion.) Since the $(NH_4)_2S$ formed is a salt, it is highly ionized, and the sulphide ion concentration is thus enormously increased, the concentration in a 0.1 molar solution of $(NH_4)_2S$ being 1.8×10^{-6}. This is so in spite of the fact that $(NH_4)_2S$ is a salt of a weak base and a weak acid and is therefore highly hydrolyzed by water.

The effect of ammonium hydroxide can be strikingly illustrated in the following manner. A tenth molar solution of $FeSO_4.7H_2O$ (27.8 g./l.) is prepared and saturated with H_2S. No precipitate results. We assume therefore that the concentrations of $S^=$ and Fe^{++} are not great enough to exceed the solubility product of FeS:

$$[Fe^{++}] \times [S^=] < K_{sp}.$$

If to this solution of $FeSO_4$, saturated with H_2S, ammonium hydroxide is added to alkalinity, a heavy precipitate of FeS forms immediately. Since the $[Fe^{++}]$ has not been changed, the $[S^=]$ must have been naturally increased by the addition of NH_4OH, in order to precipitate the FeS.

2. Question. — Explain in terms of the ionic theory why ammonium acetate is added in the test for barium, with potassium chromate.

Answer. — Whereas barium chromate is insoluble in weak acetic acid solutions, increasing hydrogen ion concentration tends to make it dissolve. This is evident from the equilibria:

$$BaCrO_4 \overset{(1)}{\rightleftarrows} BaCrO_4 \overset{(2)}{\rightleftarrows} Ba^{++} + \boxed{Cr^{=}O_4}$$

$$HAc \rightleftarrows Ac^{-} + \boxed{H^{+}}$$

$$\boxed{\phantom{H^{+}}} \rightleftarrows HCrO_4^{-}.$$

The $HCrO_4^-$ ion, representing the **secondary dissociation** of H_2CrO_4, is **weakly dissociated,** and therefore tends to form. This removal of $CrO_4^=$ ions promotes solution of the $BaCrO_4$,

since equilibra **1** and **2** shift, as previously explained for a similar case.

Any reduction in H^+ ion concentration will prevent this tendency. $NH_4C_2H_3O_2$ (or any soluble acetate) is added to reduce the H^+ ion concentration by virtue of the **common-ion effect.** This has been explained in detail (see pages 102 and 112); it will be briefly reviewed here. The equilibrium equation for acetic acid is:

$$\frac{[H^+] \times [C_2H_3O_2^-]}{[HC_2H_3O_2]} = K.$$

Since $HC_2H_3O_2$ is weakly dissociated, the addition of $NH_4C_2H_3O_2$, a highly ionized salt, greatly increases the $[C_2H_3O_2^-]$, causing a consequent large fall in $[H^+]$ to keep K constant.

Another point of view in the above case may be taken. The equilibrium involving the chromate ion is

$$H^+ + CrO_4^= \rightleftarrows HCrO_4^-;$$

the equation is:

$$\frac{[H^+] \times [CrO_4^=]}{[HCrO_4^-]} = K.$$

Increasing $[H^+]$ necessitates a decrease in $[CrO_4^=]$ and an increase in $[HCrO_4^-]$ to keep K constant. Sufficient decrease in $[CrO_4^=]$ will cause $[Ba^{++}] \times [CrO_4^=]$ to go below $K_{S.P.}$ for $BaCrO_4$, and cause solution of it. Conversely, if $[H^+]$ is decreased by the common-ion effect, $[CrO_4^=]$ will be increased and more $BaCrO_4$ precipitated.

Other Applications of the Common-Ion Effect. — While there are numerous other applications of the effect of adding a common ion, only two of them are outstanding. The first is the addition of NH_4Cl before NH_4OH in precipitating the cobalt-iron group with NH_4OH and H_2S; the second, the addition of the same reagent before precipitating the alkaline earth group with NH_4OH and $(NH_4)_2CO_3$ (if Mg is tested for with Na and K, etc.); and the third, the addition

of NH_4Cl before NH_4OH in the phosphate test for magnesium. The purpose in all three cases is exactly the same, namely, to repress the $[OH^-]$ of NH_4OH by addition of a salt of the NH_4^+ ion, so preventing premature precipitation of magnesium (see page 110 *et seq.*)

The second case of common-ion effect commonly occurring is in the separation of the phosphates of iron, chromium, and aluminium in weakly acid solution. The solution must be acid, but **almost neutral,** to precipitate $FePO_4$, $CrPO_4$, and $AlPO_4$, which are insoluble in this medium; and to prevent precipitation of $BaHPO_4$, $SrHPO_4$, $CaHPO_4$, and $MgHPO_4$, which are soluble in an acid medium. The solution is made weakly acid by adding $HC_2H_3O_2$, and the H^+ ion is then repressed by adding $NH_4C_2H_3O_2$ as previously explained.

3. Question. — When NaOH is added to a solution of $SnCl_2$, a white precipitate is first formed; this is dissolved on addition of more NaOH. Explain this phenomenon in terms of the ionic theory.

Answer. — The white precipitate formed on addition of NaOH to $SnCl_2$ is $Sn(OH)_2$, which is insoluble, but at the same time amphoteric; that is, it is capable of ionizing both as an acid and as a base, according to the following equations:

$$\begin{array}{ccccccc} & & & & \text{(solid)} & & \\ & & & & Sn(OH)_2 & & \\ \text{(acid ionization)} & & & & \Uparrow\Downarrow \text{(1)} & & \text{(basic ionization)} \\ \boxed{\begin{array}{l} 2H^+ \\ 2OH \end{array}} & + & SnO_2^= & \overset{\text{(2)}}{\rightleftarrows} & Sn(OH)_2 & \overset{\text{(3)}}{\rightleftarrows} & Sn^{++} + 2OH^-. \\ & & & & \text{(dissolved)} & & \\ & & 2Na^+ & \rightleftarrows & 2NaOH. & & \\ & & & & \text{(excess)} & & \\ \Downarrow & & & & & & \\ 2H_2O & & & & & & \end{array}$$

As the excess NaOH is added, the OH^- ions of the highly ionized NaOH unite with the H^- ions of $Sn(OH)_2$ to form **weakly ionized** H_2O. Removal of the OH^- causes undersaturation **(the S. P. Principle)** and disturbance of equilibrium **2,** with the result that more $Sn(OH)_2$ dissociates to

reëstablish equilibrium. This in turn causes disturbance of equilibria **1** and **3,** both shifting in the direction of $Sn(OH)_2$ (dissolved). If enough NaOH is added, all the $Sn(OH)_2$ (solid) will be dissolved.

Another way of viewing this case is as follows. The $[H^+]$ and $[OH^-]$ of $Sn(OH)_2$ must satisfy

$$[H^+] \times [OH^-] = K_w.$$

As $[OH^-]$ is enormously increased by addition of NaOH, $[H^+]$ must become vanishingly small to keep K constant. But the expression

$$[H^+]^2 \times [SnO_2^=] = K_{sp}$$

must also be satisfied. Since all takes place in one solution, $[H^+]$ in both cases is the same. To compensate the great diminution in $[H^+]^2$, therefore, $[SnO_2^=]$ must become much larger. This takes place through solution of more $Sn(OH)_2$, as explained above.

The $Sn(OH)_2$ solid may also be dissolved by addition of HCl instead of NaOH. The basic ionization of $Sn(OH)_2$ is affected in this case, the OH^- ions of $Sn(OH)_2$ uniting with the H^+ ions of HCl to form **weakly ionized** water. From this point the explanation follows exactly the same trend as for the addition of excess base.

As was previously mentioned, other hydroxides exhibit the same properties. The common ones are aluminium, chromic, zinc, lead, arsenious, and antimonous hydroxides. Except for variations in the equations for the reactions of these hydroxides with excess of strong base or strong acid, the explanations are all exactly similar.

The question frequently arises as to whether these amphoteric hydroxides (except zinc, which forms an ammonia-complex) will dissolve in ammonium hydroxide. The fact is that this action does take place, but only to a small extent. Let us consider the case of aluminium hydroxide with excess ammonium hydroxide:

$$\begin{array}{l} \overset{\text{(solid)}}{\text{Al(OH)}_3} \\ \uparrow\downarrow \\ \text{H}_2\text{O} + \boxed{\begin{array}{l}\text{H}^+ \\ \text{OH}^-\end{array}} + \text{AlO}_2^- \rightleftarrows \underset{\text{(dissolved)}}{\text{Al(OH)}_3} \rightleftarrows \text{Al}^{+++} + 3\text{OH}^- \\ \qquad\qquad\qquad\quad \text{NH}_4^+ \rightleftarrows \text{NH}_4\text{OH}. \\ \uparrow\downarrow \\ \text{H}_2\text{O} \end{array}$$

(The acidic dissociation of $Al(OH)_3$ is represented as shown because $Al(OH)_3$ is more likely $AlO_2H.H_2O$ than $Al(OH)_3$, according to certain investigators. It is sometimes represented as follows:

$$Al(OH)_3 \rightleftarrows AlO_3^{\equiv} + 3H^+.$$

Either is acceptable.)

It is true that apparently the same facts exist for NH_4OH as for NaOH. NH_4AlO_2, however, is a salt of a weak base and a very weak acid. The result is that it is highly hydrolyzed by water. In other words the reaction

$$NH_4^+ + OH^- + H^+ + AlO_2^- \rightleftarrows NH_4^+ + AlO_2^- + H_2O$$

goes chiefly in the (←) direction. The result is that few OH^- ions are removed, and therefore little $Al(OH)_3$ (solid) dissolved.

4. Question. — Explain in terms of theory why AgCl is dissolved by NH_4OH and reprecipitated by HNO_3 in excess.

Answer. — AgCl solid dissolves to a slight extent and ionizes as a result.

(Incidentally, insoluble material like AgCl may be considered 100 per cent ionized because of the great dilution of the solution.) The equilibria set up by AgCl are:

$$\begin{array}{l} \overset{\text{(solid)}}{\text{AgCl}} \rightleftarrows \underset{\text{(dissolved)}}{\text{AgCl}} \rightleftarrows \boxed{\text{Ag}^+} + \text{Cl}^- \\ \qquad\qquad\qquad\quad 2\text{NH}_4\text{OH} \rightleftarrows \boxed{2\text{NH}_3} + 2\text{H}_2\text{O} \\ \qquad\qquad\qquad\quad \uparrow\downarrow \qquad\qquad\quad \uparrow\downarrow \\ \qquad\qquad\qquad\quad 2\text{NH}_4^+ + 2\text{OH}^- \qquad \text{Ag(NH}_3)_2^+. \end{array}$$

Since a solution of ammonia contains dissolved ammonia gas and a small amount of ammonium hydroxide, the equilibria for ammonia and water results as shown above. Casting about for a **weakly ionized** substance, we find the complex ion $Ag(NH_3)_2^+$. Since this complex is very weakly dissociated, the NH_3 molecules and Ag^- ions unite. The result is that the latter are removed from the field of action. This causes the solution to become undersaturated with AgCl (**the S. P. Principle**), and more AgCl (dissolved) dissociates to replace the ions removed, which in turn causes solution of AgCl (solid) as explained in other similar cases.

From the point of view of the mass-action equations, we have for $Ag(NH_3)_2^+$:

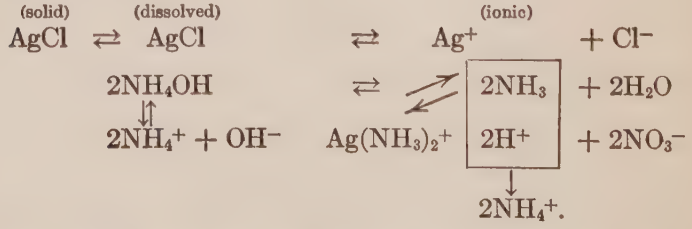
$$\frac{[Ag^+] \times [NH_3]^2}{[Ag(NH_3)_2^+]} = K.$$

The greater the $[NH_3]$, the smaller $[Ag^+]$ becomes; when $[Ag^+]$ becomes so small that it is less than the concentration necessary to equal the solubility product of AgCl, i.e., when

$$[Ag] \times [Cl] < K_{S.P.},$$

all the AgCl will be dissolved.

The effect of the addition of HNO_3 to AgCl dissolved in ammonia is manifested as follows. Considering the equilibria previously written:



When HNO_3 is added, the H^+ ion unites with the NH_3 molecules from the small dissociation of (NH_4^+). The reaction in the direction of the NH_4^+ ion is practically 100

per cent. The result is that the $Ag(NH_3)_2^+$ equilibrium is disturbed. More of the complex dissociates to replace the NH_3 removed, and thus returns Ag^+ ion to the solution at the same time. If enough HNO_3 is added, the $[Ag^+]$ will become large enough to exceed the solubility product of AgCl and the latter will be precipitated.*

It is interesting to note that, whereas AgCl can be readily and completely dissolved by ammonia, AgBr dissolves to a lesser extent, and AgI practically not at all. The reason is that the latter is so insoluble that the $[NH_3]$ manifested in concentrated ammonia does not reduce $[Ag^+]$ (see mass-action equation) below the solubility product of AgI. The magnitude of the respective solubility products indicates this:

$$\begin{aligned} AgCl &= 1.2 \times 10^{-10} \\ AgCNS &= 7.1 \times 10^{-13} \\ AgBr &= 3.5 \times 10^{-13} \\ AgI &= 1.7 \times 10^{-16}. \end{aligned}$$

* If the assumption that the H^- ion unites with the NH_3 molecule is objectionable, though it should be no more so than the union of Ag^+ ion and NH_3 molecule, the explanation may be approached at greater length with the same result, by assuming union of H^+ and OH^- ion to form water. Both probably occur.

CHAPTER VIII

QUESTIONS AND PROBLEMS

Note. — The following is a list of questions which have been selected as being representative of the types which might be asked in an elementary course in qualitative analysis. With the idea of giving the student a starting-point, but not supplying a complete answer to those questions on ionic theory which are more involved, a suggestion or a hint is given with each.

To avoid unnecessary repetition in writing the questions, the student should understand that so far as is possible the questions are to be answered in terms of the theory which has been presented. Thus, instead of saying at the beginning of each question of this nature, "Explain in terms of the Law of Mass Action and the ionic theory why AB is soluble in . . . ," etc., the question will read, "Explain why AB is soluble in . . . ," etc., unless some special case is referred to.

In addition to the questions for review and application of the ionic theory, some review questions on material presented earlier have been included.

1. Explain why AgCl is dissolved by NH_4OH and reprecipitated by HNO_3. *Hint.* — Ag forms a complex ion; H_2O is formed. (*N.B.* — This type of explanation applies as well to certain compounds of Cu, Cd, Co, Zn, and Ni.)
2. Why is it that Pb^{++} may sometimes not be precipitated by NH_4Cl when H_2S will precipitate it? *Hint.* — Compare S.P. of $PbCl_2$ and PbS.
3. Why is it that Ag is never found in the Cu group after analyzing the Ag group, but lead is always found in the Cu group if

found in the other? *Hint.* — Compare S. P. of AgCl and $PbCl_2$.

4. Why is $PbCl_2$ less soluble in a solution of NH_4Cl than in water? *Hint.* — Common ion.
5. Assuming complete ionization of $PbCl_2$, what is the solubility of this salt in a solution which is $0.5N$ in Cl^- ion? A saturated solution of $PbCl_2$ is $0.069N$ at room temperature.
6. If the total volume of the solution in question 5 were 20 c.c., how much Pb would have to be present as the nitrate in order to give a precipitate with 8 c.c. of $2N$ NH_4Cl (assuming no supersaturation, which actually occurs)?
7. Why is a considerable excess of reagent added in precipitating a given compound? *Hint.* — Common ion.
8. By means of mass-action equations, show the relation between the H^+ ion concentration and the concentration of one of the ions of the copper group, say Cd^{++}.
9. Why is PbS dissolved by boiling nitric acid and not by HCl? *Hint.* — Oxidation of the $S^=$ ion and low S. P. of PbS (same for Bi, etc.).
10. Why is $PbSO_4$ more soluble in HNO_3 than in water? *Hint.* — Compare primary and secondary ionization of H_2SO_4.
11. Explain the solubility of $PbSO_4$ in $NH_4C_2H_3O_2$. *Hint.* — $Pb(Ac)_2$ is a weakly ionized salt (exception).
12. Why can $PbCrO_4$ be precipitated from the $NH_4C_2H_3O_2$ solution which dissolved the insoluble $PbSO_4$? *Hint.* — Compare S. P. of $PbCrO_4$ with that of $PbSO_4$.
13. If Pb were not completely removed by H_2SO_4, would it be precipitated by the addition of NH_4OH in excess? *Hint.* — S. P. of $Pb(OH)_2$.
14. Why may $Cu_2Fe(CN)_6$ be precipitated from a weakly acid solution, but not from an ammoniacal one under ordinary conditions of concentration? *Hint.* — Complex ion of Cu.
15. $Cu(OH)_2$ is precipitated from a salt of Cu by NaOH. Why is it not permanently precipitated by NH_4OH? *Hint.* — Complex ion of Cu.
16. If, to the above NH_4OH solution, $(NH_4)_2S$ is added, the CuS will be precipitated. Does this indicate anything about the dissociation of the $Cu(NH_3)_4^{++}$ ion?
17. If KCN is added to a solution containing Cu and Cd ions, H_2S will precipitate the latter, but not the former. Explain. *Hint.* — Compare stability of the complex cyanide of Cu with that of Cd.

18. A solution of $BiCl_3$ in the presence of HCl gives a white precipitate when it is considerably diluted with water. Explain. *Hint.* — Hydrolysis.
19. Why does $SnCl_2$ first give a heavy white precipitate with NaOH, this precipitate then dissolving in excess of the reagent? *Hint.* — $Sn(OH)_2$ is amphoteric. (Same for Al, Zn, As, Sb, and Pb, in the lower valences of the latter three.)
20. Na_2S in solution gives a strongly alkaline reaction with litmus paper. Explain. *Hint.* — Hydrolysis.
21. Formulate the equations for the hydrolysis of Na_2S and from that draw a conclusion as to the effect of addition of a strong solution of NaOH.
22. Write the equations for the reactions between Na_2S and HCl, and between Na_2S_2 and HCl. Do the same for $(NH_4)_2S$ and $(NH_4)_2S_2$. In which direction would these reactions tend to go? Explain. *Hint.* — Dissociation of H_2S.
23. What is the basis for the separation of the Cu group of metals from the Sn group?
24. Why is Na_2S_2 or $(NH_4)_2S_2$ necessary in this separation rather than the normal sulphide of either? *Hint.* — SnS.
25. Why does As_2S_3 dissolve in $(NH_4)_2S_2$ (or Na_2S_2)? *Hint.* — $AsS_4^{\equiv}$ is a complex ion. (Same for Sb, Sn, and Hg in the case of Na_2S_2.)
26. Why does HCl precipitate As_2S_5 from $(NH_4)_3AsS_4$ or from Na_3AsS_4? *Hint.* — H_2S is weakly dissociated. (Same for Sb, Sn, and Hg.)
27. Write the mass-action equation for $MgNH_4AsO_4$. Why is the latter soluble in dilute solution of strong acids? *Hint.* — $H_2AsO_4^-$ and $HAsO_4^{=}$ are weakly dissociated.
28. It is possible to have some $SbCl_3$ in solution in the test for Sn. It is directed to add HCl to prevent precipitation of SbOCl. Explain. *Hint.* — Reverse hydrolysis.
29. NH_4OH will dissolve As_2S_5, but not HgS. Explain. *Hint.* — As forms complex sulpharsenate ions.
30. Explain the basis of the separation of HgS and As_2S_5 from Sb_2S_5 and SnS_2 by concentrated HCl. *Hint.* — Compare S. P. of the latter two with the former.
31. Explain why the phosphates of Fe, Cr, and Al are insoluble in weakly acid solution, but those of Mg, Ba, Sr, and Ca are not. *Hint.* — Compare S. P. of the former group with the latter.
32. What element of the Fe group might be precipitated with the

Cu group? Explain how this might come about. *Hint.* — Compare S. P. of the two group sulphides.

33. Why is FeS soluble in dilute HCl? *Hint.* — H_2S is weakly dissociated. (Same for the other sulphides of this group, except that CoS and NiS are slowly soluble.)
34. Why cannot Al or Cr be precipitated as sulphides in aqueous solution? *Hint.* — Hydrolysis.
35. Show by the relation of the mass-action equations for the two dissociations of $Al(OH)_3$ that the quantity of Al dissolved in the form of aluminate is proportional to the OH^- concentration.
36. Explain the basis of the separation of Zn from Fe by means of NaOH. *Hint.* — $Zn(OH)_2$ is amphoteric.
37. Explain the basis of the separation of Cr from Mn by means of Na_2O_2. *Hint.* — Formation of $CrO_4^=$ ion.
38. Iron sulphide is soluble in acetic acid; ZnS is not. Explain. *Hint.* — Compare S. P. of the two sulphides.
39. Using equilibrium equations, show why it is necessary to acidify a solution of $Al(OH)_3$ in excess NaOH before precipitating the $Al(OH)_3$ with NH_4OH.
40. $Zn(OH)_2$ is an insoluble compound, yet the separation of Al from Zn depends upon the precipitation of $Al(OH)_3$ by ammonium hydroxide in the presence of the Zn^{++} ion. Explain. *Hint.* — Zn forms a complex ion with NH_3.
41. Explain why Zn or ZnS may be precipitated from a solution in HCl to which a large quantity of $NaC_2H_3O_2$ has been added. *Hint.* — $HC_2H_3O_2$ is a weak acid.
42. Complete the following equations:

    $AlCl_3 + Na_2CO_3 + H_2O \rightarrow$
    $CrCl_3 + Na_2CO_3 + H_2O \rightarrow$
    $AlCl_3 + Na_2CO_3 + H_2O \rightarrow$

    Explain why these reactions take place. *Hint.* — Hydrolysis.
43. What reaction toward litmus would you expect the following compounds to give: $FeCl_3$, $CrCl_3$, $AlCl_3$, Na_2CO_3? Explain.
44. Would you expect arsenic (trivalent) and aluminium to be precipitated completely from their solutions by Na_2CO_3? Explain. *Hint.* — Na_2CO_3 hydrolysis. $Al(OH)_3$ and $As(OH)_3$ are amphoteric.
45. If $(NH_4)_2SO_4$ were added to the Fe group instead of NH_4Cl, what errors might be introduced? Explain.
46. Why is NH_4Cl always added before the NH_4OH at the beginning of the Fe group? Explain in detail. *Hint.* — $Mg(OH)_2$ is insoluble; common-ion effect.

47. Write the reactions for the hydrolysis of $(NH_4)_2CO_3$. What reagent could best be used to prevent this hydrolysis?
48. In what way would the hydrolysis of $(NH_4)_2CO_3$ affect the accuracy of the alkaline earth group analysis? *Hint.* — The bicarbonates of the alkaline earth metals are much more soluble than the carbonates.
49. Explain the precipitation of $SrSO_4$ by a $CaSO_4$ solution. Why is there no precipitation when the latter is added to a dilute solution of a soluble salt of Ca? *Hint.* — Compare the S. P. of the two sulphates.
50. Upon what does the separation of Ba from Sr and Ca depend? *Hint.* — Compare the S. P. of the chromates of Ba, Sr, and Ca.
51. Explain why $BaCrO_4$ is not precipitated from a solution in HCl. *Hint.* — $HCrO_4^-$ is weakly dissociated.
52. Why is $BaCO_3$ soluble in acetic acid, while CaC_2O_4 is not? *Hint.* — Compare the strengths of $HC_2H_3O_2$ and $H_2C_2O_4$.
53. In precipitating Sr as its chromate, why must the solution be alkaline and alcoholic? *Hint.* — See S. P. of $SrCrO_4$.
54. What reagent which is closely analogous could be substituted for Na_2HPO_4 in the precipitation of Mg? *Hint.* — Arsenic and phosphorus are in the same group in the periodic table.
55. Explain the solubility of $MgNH_4PO_4$ in dilute HCl. *Hint.* — The secondary and tertiary ionizations of H_3PO_4 are weak.
56. Why is $BaSO_4$ soluble in concentrated H_2SO_4? *Hint.* — $Ba(HSO_4)_2$ is more soluble than $BaSO_4$.
57. Can Mg be precipitated from a solution containing NH_4Cl by boiling with Na_2CO_3? *Hint.* — NH_4OH is unstable and Na_2CO_3 is hydrolyzed.
58. Why is $NH_4C_2H_3O_2$ added in the test for Ba? *Hint.* — Common ion.
59. Why must traces of Ba, Sr, and Ca be removed before testing for Mg?
60. Why is a strong base added in the test for the NH_4^+ ion? What other property must this base possess? *Hint.* — NH_4OH is weakly dissociated and volatile.
61. Why is $K_2NaCO(NO_2)_6$ readily soluble in dilute HCl? *Hint.* — HNO_2 is unstable.
62. Define *oxidation* and *reduction*. Write equations for five reactions in which oxidation and reduction take place. Underscore the substances oxidized and those reduced.
63. Define *valence* as applied to an oxidizing agent; a reducing agent.

64. Which of the following are oxidizing agents, which reducing: $KMnO_4$, $K_2Cr_2O_7$, H_2S, HNO_3? Write a reaction in which each acts as either an oxidizing or a reducing agent.
65. Why is Fe always in the divalent condition in the filtrate from the precipitation of the Cu and Sn groups?
66. A yellow solution containing a chromate is treated with H_2S for the precipitation of the Cu group. What changes in color, etc., take place due to the Cr? If insufficient H_2S is passed into the solution, what will be the effect on the subsequent detection of chromium?
67. An acid is 0.5*N*. To what volume must 200 c.c. be diluted to make it 0.35*N*?
68. Of a certain NaOH solution, 45 c.c. are neutralized by 35 c.c. of a 0.7*N* solution of HCl. What is the normality of the NaOH?
69. Calculate the molarity of a solution of NH_4OH of density 0.95 containing 13.3 per cent NH_3.
70. A solution of 20 c.c. of KCl gives a precipitate of AgCl which weighs 2.532 g. What is the normality of the solution with respect to KCl?
71. A solution of 4.45 g. of mannite in 250 g. of water freezes at $-$ 0.22° C. What is the molecular weight of mannite?
72. A solution of a salt which is 80 per cent dissociated contains ¼ of the molecular weight of the salt in 500 g. of water. The salt is made up of a divalent and two univalent ions. What will be the freezing-point of the solution?
73. It is desired to make 1,000 c.c. of a solution (at room temperature) with an H^+ ion concentration of 10^{-3}. Considering NaOH to be completely dissociated at this concentration, what normality of NaOH will give the desired value?
74. How much acetic acid ($N/10$) will it take to make 300 c.c. of a solution with an H^+ ion concentration of 1.5×10^{-3}?
75. If 5 c.c. of a 6*N* solution of NH_4Cl are added to 25 c.c. of a $N/10$ solution of NH_4OH, what is the concentration of the OH^- ion? Assume the NH_4Cl to be 70 per cent ionized.
76. How much of a 2*N* solution of NH_4OH will be necessary to start the precipitation of $Mg(OH)_2$ from 40 c.c. of a $N/10$ solution? Assume that the NH_4OH is 1.0 per cent ionized, and that there is no increase in volume of the solution on addition of the NH_4OH.
77. $MgCO_3$ dissolves to the extent of 4.3×10^{-1} g. per liter at room temperature. Assuming that it is completely ionized at this concentration, calculate its solubility product.

78. Calculate the concentration of the H^+ ion in a $N/10$ solution of NH_4OH which is $N/100$ with respect to NH_4NO_3. Assume the latter to be completely dissociated.
79. A solution containing 2.5 c.c. of $12N$ HCl in a total volume of 100 c.c. is saturated at room temperature with H_2S to precipitate its CuS. The CuS is filtered, and the solution evaporated to dryness. Calculate the amount of $CuCl_2$ that remains in the residue. The S. P. for H_2S is 1.1×10^{-23} and that of CuS is 8.5×10^{-45}.

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